Draft
Technical Support Document for HWC MACT Standards

Volume IV:

Compliance with the Proposed MACT Standards

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) regulates the burning of hazardous waste in incinerators under 40 CFR Part 264/265, Subpart O and in boilers and industrial furnaces under 40 CFR Part 266, Subpart H. The Agency is proposing revised regulations applicable to these hazardous waste combustion devices. This document provides technical background for the continuous emission monitoring and operating limits requirements in the proposed rule.

In support of the proposed rule EPA has surveyed the state-of-the-art of continuous emissions monitoring systems (CEMS) technology for monitoring for particulate matter (PM), mercury, acid gases (HCl and Cl_2), multi-metals, and organics. In addition, EPA has drafted performance specifications and data quality assurance requirements for PM, mercury, acid gas, and multi-metals CEMS. EPA has also carried out a preliminary CEMS testing program designed to assess the likelihood of CEMS being available that are suitable for compliance monitoring. Based on the CEMS assessments in the surveys, the results available to date from the preliminary testing program, and cost-effectiveness considerations, EPA plans to require CEMS only for PM and total mercury. Monitoring of acid gases and multi-metals will be optional. A formal demonstration of PM and mercury CEMS is planned in order to verify that instruments are available that can meet the proposed performance specifications and thus be used for compliance monitoring.

Compliance with emission limits for those pollutants that are not monitored directly at the stack will be achieved through the monitoring of certain system operating parameters that affect emissions levels (possibly in conjunction with indirect surrogate continuous monitoring). System operating parameters will be chosen which are indicative of the day-to-day operation and performance of the hazardous waste burner. This document includes procedures to adjust and control the operating parameter, procedures to measure and monitor the operating parameter, procedures to comply with the operating parameter limit (e.g., monitoring and averaging requirements), and procedures to set the operating parameter limit (e.g., based on comprehensive performance tests or equipment manufacturer and/or designer specifications).

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NOMENCLATURE

ACA	Absolute Calibration Audit
AES	Atomic Emission Spectroscopy
APCD	Air Pollution Control Device
APCS	Air Pollution Control System
BIF	Boiler and Industrial Furnace
BTF	Beyond The Floor
CAAA	Clean Air Act Amendment
CD	Calibration Drift
CE	Calibration Error
CEMS	Continuous Emission Monitoring System
CFR	Code of Federal Regulations
CIF	Carbon Impregnated Filter
DL	Detection Limit
DOAS	Differential Optical Absorption Spectroscopy
DOD	Department of Defense
DOE	Department of Energy
ECD	Electron Capture Detector
EPA	Environmental Protection Agency
ESP	Electro-Static Precipitator
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
FTIR	Fourier Transform Infrared
GC	Gas Chromatograph
GCP	Good Combustion Practice
GFC	Gas Filter Correlation
HAP	Hazardous Air Pollutant
HC	Hydrocarbon
HWC	Hazardous Waste Combustor
HWI	Hazardous Waste Incinerator
ICP	Inductively Coupled Plasma
IMS	Ion Mobility Spectroscopy
ISE	Ion Selective Electrode

LED	Light Emitting Diode
LIF	Laser Induced Fluorescence
LVM	Low Volatility Metal
LWAK	Light Weight Aggregate Kiln
MACT	Maximum Achievable Control Technology
MS	Mass Spectroscopy or Spectrometer
MWC	Municipal Waste Combustor
NDIR	Non-Dispersive Infrared
NIST	National Institute of Standards and Technology
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Poly-Chlorinated Benzene
PCDD	Poly-Chlorinated Di-benzo Dioxin
PCDF	Poly-Chlorinated Di-benzo Furan
PIC	Product of Incomplete Combustion
PM	Particulate Matter
RA	Relative Accuracy
RATA	Relative Accuracy Test Audit
RCA	Response Calibration Audit
SBIR	Small Business Innovative Research (grant)
SVM	Semi Volatile Metal
SVOC	Semi Volatile Organic Compound
TUV	German “Technical Inspection Agency”
UV	Ultra-Violet
VOC	Volatile Organic Compound
VOST	Volatile Organic Sampling Train
WESP	Wet Electro-static Precipitator
XRF	X-ray Fluorescence
ZD	Zero Drift

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CHAPTER 1

INTRODUCTION

1.0 BACKGROUND

The U.S. Environmental Protection Agency (EPA) regulates the burning of hazardous waste in incinerators under 40 CFR Part 264/265, Subpart O and in boilers and industrial furnaces under 40 CFR Part 266, Subpart H. The Agency is proposing revised regulations applicable to these hazardous waste combustion (HWC) devices. This document provides technical background for the continuous emission monitoring and operating limits requirements in the proposed rule.

This document is the fourth in a series of seven volumes of technical background documents for the rule. These include:

Technical Support Document for HWC MACT Standards, Volume I: Description of Source Categories, which provides process descriptions of major design and operating features including different process types and air pollution control devices currently in use and potentially applicable to various combustion source categories; description of air pollution control devices including design principles, performance and operating efficiency, process monitoring options, and upgrade/retrofit options; and major source determination for all sources including a discussion on the methodology used to estimate annual emissions, assumptions used, and an emissions summary for each source listing each HAP.

Technical Support Document for HWC MACT Standards, Volume II: HWC Emissions Data Base, which contains a summary of the emissions information on toxic metals, particulate matter (PM), HCl and Cl_2, hydrocarbons, carbon monoxide, semi-volatile and volatile organic compounds, and dioxins/furans from HWCs. Other detailed information encompassed in the data summary include company name and location, emitting process information, combustor design and operation information, APCD design and operation information, stack conditions during testing, feed stream feed rates, and emissions rates of HAPs by test condition.

Technical Support Document for HWC MACT Standards, Volume III: Selection of Proposed MACT Standards and Technologies, which identifies the MACT floor for each HAP and source category for existing sources and new sources and discusses the approach used to define the floor and beyond-the-floor alternatives considered for the proposed rule.

Technical Support Document for HWC MACT Standards, Volume IV: Compliance with the Proposed HWC Standards, which contains detailed discussions of continuous emissions monitors and operating limits for the proposed rule.

Technical Support Document for HWC MACT Standards, Volume V: Engineering Costs, which contains the cost estimates for APCD requirements for existing and new facilities to meet the proposed emissions standards.

Technical Support Document for HWC MACT Standards, Volume VI: Development of Comparable Fuels Specifications, which summarizes the composition including hazardous species in benchmark fossil fuels such as gasoline, #2 fuel oil, #4 fuel oil, and #6 fuel oil. This information is being used to develop specifications which EPA is considering to allow comparable fuels to be excluded from the definition of hazardous waste.

Technical Support Document for HWC MACT Standards, Volume VII: Miscellaneous Technical Issues, which provides additional information on several topics such as the treatment of measurements below analytical detection limits, the procedures for handling missing data, and the rationale for grouping metals of similar volatility. The impact of these methodologies on the proposed MACT limits, the cost estimates, and the national emissions estimates are also discussed.

In addition to these technical background documents, a companion Regulatory Impact Analysis report has been prepared in support of the rule.

Emission standards are being proposed for three types of hazardous waste incineration facilities:

- Cement Kilns
- Lightweight Aggregate Kilns

- Incinerators (On-site and Commercial)

The hazardous air pollutants for which emission standards are proposed are:

- Mercury (Hg)
- Low Volatility Metals (LVM)
- Semi-Volatile Metals (SVM)
- Particulate Matter (PM)
- Hydrochloric Acid and Chlorine as Total Chlorine (HCl/Cl_2)
- Carbon Monoxide (CO)
- Hydrocarbons (HC)
- Dioxins/Furans (PCDD/PCDF)

These emission standards are being developed through the "maximum achievable control technology" (MACT) approach defined in Title 3 of the 1990 Clean Air Act Amendments (CAAA). In this approach the MACT floor standard for existing facilities is established at the level of the average performance of the best 12% of existing sources. Depending on the additional benefits and costs, EPA may elect to set more stringent, but technically achievable, beyond-the-floor (BTF) standards for specific HAPs. In the proposed rule, BTF standards have been set for PCDD/PCDF and for Hg for all HWC source categories, and BTF standards have been proposed for HCl/Cl_2 for LWAKs only.

The proposed floor and BTF standards have been selected based on a database (described in Volume II) of trial burn and compliance test emissions measurements from 77 incinerators, 35 cement kilns, and 12 lightweight aggregate kilns using a process described in detail in Volume III. The MACT floor has been set based on the determination that the CAAA requirement of meeting the average performance of the best 12% (or top 5 if there are fewer than 30 sources) can be interpreted to mean the day-to-day performance achievable by the worst sources having the technologies represented by the top 6% (or top 3) sources. This is called the "6% Floor" and is the one ultimately selected for the proposed rule. It was selected because it ensures that all facilities with the MACT technology can meet the MACT floor.

1.1 CONTINUOUS EMISSION MONITORING

In order to determine which continuous emission monitoring systems (CEMS) will be available and demonstrated for compliance monitoring EPA has followed a strategy consisting of four main elements. First, EPA has surveyed the state-of-the-art of CEMS technology for monitoring for particulate matter (PM), mercury, acid gases (HCl and Cl_2), multi-metals, and

organics. Second, EPA has drafted performance specifications and data quality assurance requirements for PM, mercury, acid gas, and multi-metals CEMS. Organics CEMS are not included because there is insufficient data to set an emission limit on individual organic compounds at this time. Thus performance specifications would be in place for CEMS which monitor all of the regulated pollutants (regardless of whether or not monitoring is required in the final rule). Third, EPA has carried out a preliminary CEMS testing program designed to assess the likelihood of CEMS being available that are suitable for compliance monitoring. Fourth, EPA will carry out a formal demonstration of PM and mercury CEMS to verify that instruments are available that can meet the performance specifications and thus be used for monitoring.

Based on the CEMS assessments in the surveys and the results available to date from the preliminary testing program, EPA plans to require monitoring of PM and total mercury. Monitoring of acid gases and multi-metals will be optional, and there will not be any provision for monitoring individual organic compounds. It is for this reason that only PM and mercury monitors are included in the formal demonstration program. In the following sections of the introduction, the four elements of EPA's strategy will be outlined in greater detail. The surveys, performance specifications, and descriptions of the testing program, complete with results to date, comprise the remaining sections of this document. The findings and conclusions are summarized in the final section of this introduction.

1.1.1 Survey's

EPA's state-of-the-art CEMS surveys were conducted for multi-metals, PM, mercury, acid gases, and organic compounds. Continuous monitoring, in its purest sense, implies continuous sampling and continuous reporting. However, since technology capable of this level of performance may not be available for all pollutants in the immediate future, "continuous" for the purposes of these survey's is taken to mean only that sampling should be continuous, while analysis, which should be on-site and integral to the CEMS, can be batch. Thus the desired attributes of a CEMS are: continuous sampling of emissions, as close to real-time reporting as is practical, and automated, low-cost operation. In addition, detection must be low enough to assure compliance with regulatory limits. The objective of the survey's was to identify the state-of-the-art monitoring technology, either commercially available or under development. In the case of technology under development, the status of the development effort was assessed. In either case, the laboratory and field testing track record of the CEMS was included in the survey and as part of the assessment. Each CEMS technology included in the survey was described and information on performance noted (particularly detection limits). The advantages and disadvantages of each technology were then summarized. Each survey was then concluded with an assessment of whether or not there were: 1) monitors available that had been proven capable

of providing compliance monitoring; 2) monitors available and likely to be capable of providing compliance monitoring, but unproven; or 3) monitors under development that were likely to be capable of providing compliance monitoring. In the case of the latter, some estimate of when the monitors might be available was also made. The survey's of the various CEMS comprise Chapter 2.

1.1.2 Performance Specifications And Data Quality Assurance

Draft performance specifications have been written for multi-metals, mercury (total), PM, HCl, and Cl_2. In addition, existing performance specifications for O_2, CO, and total hydrocarbon have been revised. The new performance specifications have followed the existing Performance Specification 2 for NO_x and SO_2 CEMS (40 CFR part 60, Appendix B) in order to ensure consistency. In the absence of operational data from most of these CEMS, the specifications that are required represent the minimum level of performance that can be accepted from a CEMS used for monitoring purposes.

The draft data quality assurance requirements closely follow 40 CFR part 60, Appendix F. Daily calibration and zero drift checks are required. Accuracy audits are performed on a quarterly basis with NIST traceable calibration standards and on a one to three year basis against EPA reference methods (depending on the CEMS). The draft performance specifications and data quality assurance requirements are discussed in more detail in Chapter 3, and the full texts can be found in the appendices.

1.1.3 Preliminary Test Program

The preliminary test program is aimed at providing additional field data with which to assess the feasibility of using certain CEMS for compliance monitoring. In this program, CEMS data and reference method data taken simultaneously are compared at as many conditions as possible within the scope of the testing. Since the CEMS testing is an addition to a larger program aimed at evaluating pilot scale air pollution control equipment, the scope of the testing is defined not by the CEMS evaluation but by the needs of the pilot scale evaluation.

The preliminary CEMS evaluation program will consist of tests conducted at three different sites. The first test was conducted in March of 1995 at the Rollins Environmental Services commercial waste incineration facility at Bridgeport, NJ. This facility uses a wet air pollution control system (APCS) consisting of a saturator (rapid quench), packed tower absorber, high energy venturi scrubber, and a mist eliminator. The stack gases are thus cool and saturated. Three different PM CEMS were evaluated at this facility. The results of this test are described in

Chapter 4. The second test was conducted at the Lafarge Cement Co, Freedonia, KS facility in June and July of 1995. This facility uses an APCS consisting of an ESP only. The stack gases are thus hot (350 F). Two PM CEMS were tested at this facility, as well as a mercury monitor, an organics monitor, and a PAH monitor. The results of this test are not yet available. The final test is planned to take place at the Medusa Cement Co. facility in Wampum, PA in November and December of 1995. Tentative plans call for the evaluation of two mercury monitors, an organics monitor, and an Opsis system capable of measuring Cl_2 and elemental mercury.

1.1.4 Demonstration Test Program

The CEMS demonstration test program is aimed at verifying that at least one CEMS of each type can meet the proposed performance specifications. Since the only new CEMS to be required would be for PM and total mercury, these are the only two types that will be evaluated in this program, if funds are available. The program will be conducted in two phases: 1) a demonstration test and 2) a long term endurance test. The demonstration test will involve installing the CEMS and carrying out all the tests prescribed in the performance specifications just as if the facility were buying and installing the CEMS for compliance purposes. CEMS performance in all areas covered by the performance specifications will be evaluated. The long term endurance test will involve evaluating one CEMS for at least six months. Accuracy will be checked periodically, and the daily drifts will be recorded. In addition, the maintenance record of the CEMS will be noted and evaluated. Participation in these tests will be by selection based on proposals received in response to notices placed in the Federal Register and the Commerce Business Daily. The demonstration program, announcement, and selection criteria are described in detail in Chapter 4.

1.1.5 Summary

The results of the CEMS surveys and preliminary testing can be summarized as follows.

- CEMS for PM
  - · Monitors are commercially available
  - · Several monitors have been certified by TUV (German “Technical Inspection Agency,” similar to underwriter’s Laboratories, and charged with certifying environmental monitoring instruments)
  - · They are used for compliance in Germany
  - · Indications from the test at Rollins are not conclusive, but monitoring appears feasible
  - · Conclusion: compliance monitoring appears to be feasible with currently

available instruments

- CEMS for total mercury
  - · One monitor is commercially available
  - · Several other monitors are under development, and will be available soon.
  - · The one monitor that is available is nearing TUV certification
  - · Conclusion: compliance monitoring appears to be feasible with currently available instruments

- CEMS for HCl
  - · Monitors are commercially available
  - · Several monitors have been certified by TUV
  - · They are used for compliance in Germany, and at municipal waste incinerators in this country
  - · Several monitors have been evaluated by the EPA
  - · Conclusion: compliance monitoring is feasible with currently available instruments

- CEMS for Cl_2
  - · At least one monitor is commercially available
  - · This monitor has TUV certification, but not for measuring Cl_2
  - · Conclusion: compliance monitoring appears to be feasible with currently available instruments. Need field testing to be sure.

- CEMS for Multi-metals
  - · Several technologies are under development, none close to being commercially available
  - · Several prototypes will be field tested in July-August of 1995 by EPA/DOE
  - · Conclusion: compliance monitoring appears to be feasible, but results of prototype tests are required to verify this. Performance of integrated, manufactured instruments is unknown. It will be several years before multi-metals CEMS become commercially available.

- CEMS for Organic Compounds
  - · One mass spectrometer based monitor is commercially available
  - · Several others are under development and are close to being available
  - · Need field testing to evaluate
  - · Several instruments will be field tested by EPA/DOE in July-August of 1995

· Conclusion: compliance monitoring appears to be feasible for VOC's, maybe for some SVOC's, but results of field tests are required to verify this. Many instruments will be available soon.

Thus, monitoring with currently available instruments has been demonstrated for PM and HCl, and is being demonstrated for total mercury. These demonstrations have all been carried out in Germany. Since Cl_2 monitoring can be accomplished using an established instrument, it is likely that this CEMS could also be successfully demonstrated. For cost-effectiveness considerations, however, EPA plans to require CEMS only for PM and total mercury.

1.2 OPERATING LIMITS

The preferred method for real-time assurance of compliance with flue gas maximum achievable control technology (MACT) emissions standards is the use of direct hazardous air pollutant (HAP) flue gas continuous emissions monitoring techniques. However, as discussed in above, for many HAPs, direct monitors are neither available nor cost effective. Thus, monitoring of certain system operating parameters that affect HAP emissions levels is used (possibly in conjunction with indirect surrogate HAP continuous monitoring) to ensure compliance with the emissions standards. System operating parameters are chosen which are indicative of the day-to-day operation and performance of the hazardous waste burner system. In the following sections, operating parameters that potentially affect the emissions of each of the HAPs are discussed, including:

- Rationale for consideration (or rejection) of the operating parameter.
- Procedures to adjust and control the operating parameter, if appropriate.
- Procedures to measure and monitor the operating parameter, including measuring location, if appropriate.
- Procedures to comply with the operating parameter limit (e.g., monitoring and averaging requirements).
- Procedures to set the operating parameter limit (e.g., based on comprehensive performance tests or equipment manufacturer and/or designer specifications).

System operating parameters that are considered include those related to the combustor feedstreams (e.g., composition, feedrate), the combustion chamber (e.g., temperature, pressure,

flowrate), as well as the individual components of the air pollution control system. The air pollution control device operating parameters that are discussed below are generic or typical parameters for which required limits are recommended. However, because air pollution control device operations and designs vary (even within similar type categories such as wet scrubbers), the appropriateness of these parameters should be considered and determined on a site-specific basis. This is consistent with the previous Boilers and Industrial Furnaces (BIF) rule (U.S. EPA, 1992) which states, "other air pollution control systems not explicitly mentioned in the BIF rule may require different monitoring and interlock parameters, as determined on a case-by-case basis." For more information on the design and operation of all of the combustion and air pollution control devices discussed below, refer to *Technical Resource Document for HWC MACT Standards, Volume I: Description of Source Categories*.

This volume lists and discusses the proposed operating limit parameters and monitoring requirements. It draws heavily (but not exclusively) from the precedents set by the *Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations* (U.S. EPA, 1992) and by the *EPA Handbook: Guidance on Setting Permit Conditions and Reporting Trial Burn Results Volume II of the Hazardous Waste Incineration Guidance Series* (U.S. EPA, 1989). The following chapters provide detailed discussions of:

- Averaging periods considered for compliance with operating parameter limits.

- Procedures to set operating parameter limits.

- Operating parameters to control stack gas emissions of:

  -- Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF)
  -- Particulate matter (PM)
  -- Mercury (Hg)
  -- Semi-volatile and low-volatile metals (SVM and LVM)
  -- Total chlorine
  -- Fugitives

1.3 REPORT ORGANIZATION

This report consists of 11 additional chapters. A brief description of each chapter is provided below.

Chapter 2: Presents the state-of-the-art CEMS surveys that were conducted for multi-metals,

PM, mercury, acid gases, and organic compounds. Also included in this chapter under the PM CEMS subsection is a report on a fact finding trip to Germany and an analysis of some German PM CEMS performance data.

Chapter 3: Summarizes the proposed CEMS performance specifications and data quality assurance requirements.

Chapter 4: Describes the preliminary CEMS test program and the planned demonstration test program for PM and total mercury CEMS. All results obtained to date in the preliminary test program are presented in this chapter also.

Chapter 5: A discussion of the different operating parameter averaging periods that are considered.

Chapter 6: A discussion of the procedures that are used to set limits on the operating parameters.

Chapter 7: A discussion of the operating parameters that are related to the control of PCDD/PCDF emissions.

Chapter 8: A discussion of the operating parameters that are related to the control of PM emissions.

Chapter 9: A discussion of the operating parameters that are related to the control of Hg emissions.

Chapter 10: A discussion of the operating parameters that are related to the control of LVM and SVM emissions.

Chapter 11: A discussion of the operating parameters that are related to the control of chlorine emissions.

Chapter 12: A discussion of the operating parameters that are related to the control of fugitive emissions.

Appendix A: Performance Specification for PM CEMS

Appendix B: Performance Specification for Mercury CEMS

Appendix C: Performance Specification for HCl CEMS

Appendix D: Performance Specification for Cl_2 CEMS

Appendix E: Performance Specification for Multi-metals CEMS

Appendix F: Performance Specification for O_2 and CO CEMS

Appendix G: Performance Specification Total Hydrocarbon CEMS

Appendix H: Data Quality Assurance Requirements

CHAPTER 2

CEMS SURVEYS

2.0 INTRODUCTION

Surveys of state-of-the-art technology for continuous monitoring of PM, mercury, acid gases, multi-metals, and organic compounds are described in the following sections. These surveys draw primarily upon direct communications with vendors and developers, and upon product literature. Each survey provides a discussion of the technical approaches available or being pursued to make the measurement, the capabilities, advantages, and disadvantages of each approach, the developmental status of each approach, and the certification testing history, if any, of each approach. Each survey then ends with an assessment of the feasibility of using CEMS for compliance monitoring.

2.1 CEMS FOR PARTICULATE MATTER

2.1.1 Introduction

Current measurements of particulate matter are made using EPA Method 5. Method 5 involves isokinetic sampling of the stack flow and collection of particles on a filter. The filter is then weighed to determine the mass emission rate of particulate matter. This method is a manual method and involves time consuming analysis that provides a direct measurement of the mass of emitted particulate matter (PM). A need therefore exists for a PM measurement technology that is continuous, automatic, and provides real-time analysis. The output of such a PM CEMS should be indicative of the PM mass emission rate.

Potential PM CEMS employing a variety of measurement principles are currently commercially available. None of these devices have received EPA approval for stack PM mass emissions monitoring. This is due to the fact that most of these devices actually measure secondary properties of particles from which the mass may be inferred rather than making a direct measurement of mass. For example, optical methods measure the attenuation or scattering of light

due to the presence of PM. The measurement is directly related to the volume of PM present, although in general it also depends on the PM size distribution and composition. The resultant volume measurement must then be related to mass by assuming a particle density. This is typically accomplished using a site specific calibration against Method 5. Inherent in this approach is the assumption that the relation between the measured response and PM mass loading does not change with time.

Commercially available PM CEMS are summarized in Table 2-1. This table includes all of the approaches to a PM CEMS identified based on available information. Specific manufacturers of each type of device are listed in the table as representatives of their respective technologies, thus this table is not intended to be a comprehensive compilation of vendors. Device types listed in the table are categorized as O for optical, E for extractive (PM is sampled isokinetically), and P for probe (particles make physical contact with a probe inserted into the flow). The oscillating element system (the only direct mass measurement system) is designed for ambient sampling, and is probably not suitable for application to stack sampling for the reasons discussed in Section 2.2.10. All of the other approaches are available for stack sampling, thus there is no development time connected with these technologies.

In the sections that follow, the technologies identified above are assessed in terms of their measurement ranges and sensitivities to parameters other than particulate mass loading which can give rise to biases in the measurement. In addition, the German experience with light scattering CEMS for compliance monitoring of PM emissions is discussed based on a fact finding trip to Germany and a TUV certification report for the Sick RM200.

2.1.2 Opacity Monitors

A variety of optical approaches to the problem of particulate mass measurement exist. The simplest is opacity monitoring, in which the attenuation of a light beam caused by scattering and absorption is measured. This attenuation is dependent on both the composition and size of the particles (Jahnke, 1984). Studies have shown that opacity can be correlated with mass emissions, however, concern about the stability of the correlation has prevented the use of opacity for the monitoring of mass emissions in the US (Conner and Knapp, 1988 and Conner et al., 1979). Instead, monitoring opacity for compliance purposes without any attempt to relate it to actual PM emissions is required in instances where continuous monitoring is desired. Opacity monitors are the least sensitive of the various optical approaches, with a typical range of applicability of 0.02 to 4 gr/dscf, due to the fact that a small change (attenuation) in a large quantity (the light beam transmitted across the duct) is measured (Monitor Labs, 1994).

Disadvantages:

- Insufficient sensitivity

Advantages

- Established technology, reliable operation

2.1.3 Time Dependent Optical Attenuation

A variant of the opacity meter is commercially available from BHA. This instrument monitors the time dependent component of the transmission signal, essentially measuring the change in transmission as each particle passes through the beam (Bock, 1993 and BHA Group, Inc., 1994). This approach is not sensitive to buildup on the windows, and has an upper limit on particle loading of about 4 gr/ft^3. The lower detection limit is about 4×10^{-6} gr/ft^3. The particle size range over which the instrument can effectively make measurements is 0.3 to over 75 µm. This is a cross-stack measurement requiring two points of access.

Advantages:

- Excellent sensitivity
- Continuous
- In-situ

Disadvantages:

- Sensitive to particle size distribution and particle characteristics
- Does not measure mass, must be calibrated against Method 5

2.1.4 Forward Light Scattering

Techniques that monitor particle loading by measuring the scattered light in addition to the transmitted intensity are also available. When the light scattered by many particles present in the beam is measured, the technique is referred to as ensemble scattering. Insitec has a system known as TESS (Transform method for Extinction-Scattering with Spatial resolution) that operates on this principle. A probe containing the optics is inserted into the flow, and the forward light scattering from particles passing through a slot in the probe is measured. The particle size range of the device is specified as submicron to 20 microns, and is specified as being independent of particle

size and composition. In fact, the measured scattering is used to calculate an average particle size independent of knowledge of the particle size distribution. Combined with the extinction measurement, total particle volume can then be calculated. To obtain particle mass, the technique must be calibrated against Method 5. The range of PM loadings for which the method is applicable is roughly 0.006 to greater than 1 gr/dscf. Insertion of a probe requires only one point of access to the stack (Insitec Measurement Systems, 1994).

Advantages:

- Continuous
- In-situ
- Compared to other optical methods, reduced sensitivity to particle distribution and particle characteristics

Disadvantages:

- Less sensitive than other light scattering approaches
- May not detect particles < 1 µm
- Some sensitivity to particle distribution and particle characteristics, especially if particle size falls outside of the 1 to 20 µm range
- Does not measure mass, must be calibrated against Method 5

2.1.5 Backward Light Scattering

An instrument using back scattered light is available from Environmental Systems Corporation. This instrument, known as the P5A particulate monitor, has a roughly constant response to particles in the 0.1 to 10 µm range. The response of the instrument does depend on the optical properties of the particles, and a mass measurement is made by calibration against Method 5. This instrument has a PM range of 0.0005 to 8 gr/dscf and requires only one point of access to the stack (Environmental Systems Corporation, 1994).

Advantages:

- Good sensitivity
- Sensitive to particles as small as 0.1 µm
- Continuous
- In-situ

Disadvantages:

- Sensitive to particle distribution and particle characteristics, especially if particle size falls outside of the 0.1 to 10 µm range
- Does not measure mass, must be calibrated against Method 5

2.1.6 90° Light Scattering

A German company, Sick Optic, makes a PM CEMS based on light scattering at 90°. This device, the RM200, only requires one point of access to the stack, and has a PM detection limit of $2x10^{-6}$ gr/dscf (Sick Optic-Electronic, Inc., 1994). The particle size range to which the device is sensitive is 0.1 to 50 µm. This device is likely to be sensitive to particle size distribution and particle properties, and requires site specific calibration in order to make PM mass emission measurements. It use has been approved by the German equivalent of the EPA, and it has passed the German TUV standards. It is installed on between one and two hundred stacks. A site specific calibration is required in each case in order to provide PM mass emissions.

Advantages:

- Excellent sensitivity
- Sensitive to particles as small as 0.1 µm
- Continuous
- In-situ

Disadvantages:

- Sensitive to particle distribution and particle characteristics, although the Germans have evaluated the performance and found it to be adequate
- Does not measure mass, must be calibrated against Method 5

2.1.7 Triboelectric Effect

The triboelectric effect is the transfer of electric charge when particles impact on a dissimilar object. The measurement thus consists of inserting a metal rod into the flow and measuring the electric current induced by the particles as they flow past and hit the rod. This technology is currently available from Auburn International for monitoring flow upsets and bag breakthroughs (Auburn International Inc., 1994). When calibrated against Method 5, particle mass flow rate can be estimated (Averdieck, 1987). The magnitude of the effect is dependent on

composition, size, flow velocity (small particles follow streamlines and do not impact the probe), and resistivity (which is highly dependent on humidity). Response is also sensitive to conditioning of the probe surface through the buildup of deposits and/or erosion (Gnyp et al., 1979, John, 1975, John et al., 1980, and Gruber and Bastness, 1973).

Advantages:

- Excellent sensitivity (detection limit $5x10^{-5}$ gr/dscf)
- Sensitive to particles as small as 0.5 µm
- Continuous
- In-situ

Disadvantages:

- Sensitive to flow velocity, particle size distribution and particle characteristics
- Does not measure mass, must be calibrated against Method 5
- Very sensitive to changes in humidity

2.1.8 Beta Transmissivity

A French company, Emissions SA, makes a beta gauge (Beta 5M) for stack sampling of PM emissions. This device uses a heated sampling probe to obtain an isokinetic sample (isokinetic sampling is maintained automatically). The sample is collected on a filter, which, at the end of the sampling period, is moved (using a continuous filter tape mechanism) to a measurement location between a carbon 14 beta particle source and a detector. The beta transmission through each blank filter is determined before sampling begins. The sampling duration is programmable and determines the mass concentration detection limit. At high PM loadings it must be kept small enough to prevent sampling excessive amounts of particulate, and is usually set at two minutes for typical applications. Analysis takes six minutes. At the end of each sampling period, the probe nozzle is temporarily closed, opened, and closed again in order to re-entrain any particulate that may have deposited in the probe (Emissions S.A., 1994).

Advantages:

- Excellent sensitivity, DL = $1.7X10^{-6}$ gr/dscf for a one hour sample
- Sensitive to all particles

Disadvantages:

- Extractive: potential problems with fallout of PM in the probe
- Batch sampling, not continuous

2.1.9 Acoustic Energy Monitoring

Jonas Inc. markets a device based on acoustic energy monitoring. In this technique shock waves caused by the impact of particles with a probe inserted into the flow are used to measure particle loading. The device counts the number of impacts and also measures the energy of each impact. This information, coupled with knowledge of the flow velocity, allows calculation of the particle mass (Jonas, Inc., 1994 and Jonas, 1990). Since the probe distorts the flow, changes in flow velocity and particle size distribution will, in principle, change the instrument response.

Advantages:

- Good sensitivity, DL not known, but range specified as 0 to 0.05 gr/dscf
- Continuous
- In-situ

Disadvantages:

- Not as sensitive to small particles less than 10 µm
- Sensitive to flow velocity and particle size distribution
- Does not measure mass, must be calibrated against Method 5

2.1.10 Tapered Oscillating Element Microbalance (TOEM)

Rupprecht and Pataschnick Co., Inc. make an ambient air monitor based on a TOEM. In this technique the natural frequency of oscillation of a beam is measured as particles accumulate on a filter through which the sampled air flow passes (the changing mass changes the frequency of oscillation). This is thus a direct measurement of particle mass. However, the instrument response is humidity and temperature dependent, requiring control of these two parameters. The filter also requires periodic changing: for the device as currently configured, a 0.005 gr/dscf PM loading would require a filter change every two hours with a ½ to 2 hour downtime after each filter change. It is questionable whether this device could be made suitable for stack monitoring, and the manufacturer has no current plans to do so (Ruprecht and Pataschnick, 1994).

Advantages:

- Direct measurement of mass
- Excellent sensitivity
- Sensitive to all particles

Disadvantages:

- Extractive: potential problem with PM fallout in the probe
- Frequent downtime for filter change and re-equilibration

2.1.11 Summary

The performance capabilities and issues affecting accuracy of the various PM CEMS are summarized in Table 2-2 and Table 2-3. Opacity monitors and the tapered oscillating element device have been omitted from the table due to their lack of sensitivity and lack of availability and suitability for stack monitoring, respectively.

The response of light scattering based systems is typically a function of particle size and material properties, although less so than for opacity based systems (Gnyp et al.,1979). Specific devices are designed to have as nearly flat a response as possible over as large a portion of the size range of interest as possible. However, this does not eliminate the potential dependence of the device response on particle size distribution. Demonstration is thus required to show that the variability of particle size distribution of the source does not unduly affect the accuracy of the measurement. Further, the responses of some optical techniques depend to varying extents on the particulate composition (through its effect on the index of refraction of the particulate). Particulate composition also affects the accuracy of all optical approaches through its effect on particle density.

Devices that rely on the contact of particles with a physical probe will also have a response that is dependent on particle size for two reasons. First, smaller particles follow the flow streamlines better than large particles, and will thus tend to impact the probe less frequently. This effect will also depend on flow velocity, and results in the under-sampling of small particles. Second, small particles will have a reduced physical effect when they do impact the probe, and thus there will be a minimum detectable particle size. At what point these effects become important compared to the range of particle size that is actually present will determine the importance of size dependent response in limiting the accuracy of the measurement.

2.1.12 PM CEMS Use in Germany

In the case of PM CEMS, devices are commercially available and installed on stacks world wide. They are installed and used for compliance purposes in Germany. In fact, the Germans have taken the lead in the development, certification, and application of PM CEMS. Therefore, as part of EPA's assessment of PM CEMS for compliance, a fact-finding trip to Germany in November of 1994 was undertaken in order to investigate the nature of the German experience with PM CEMS, their certification procedure, and their use in practice for emissions compliance. The aims of the trip were the following: to bring back an understanding of the German certification process (how exhaustive and rigorous, what is required, etc.); to find out how CEMS are used for compliance in Germany; to asses CEMS reliability; and to examine German data or experience regarding the stability of the CEMS calibrations.

In order to attempt to achieve these aims, Mr. Buhne of TUV Rheinland in Cologne was visited. TUV stands for the German equivalent of "technical inspection agency." TUV, which is a non-profit organization, is mandated by the government to, among other things, perform environmental testing and the certification of CEMS which are used for environmental monitoring. TUV, and Mr. Buhne in particular, have developed both the German manual methods for PM measurement and the certification process for PM CEMS, and Mr. Buhne has extensive experience built up over 20 years with the performance of PM CEMS in the field. The meeting with Mr. Buhne was held on November 8, 1994, and the information that he related during the interview is summarized below.

In the 1960's TUV first investigated CEMS for PM. Eight devices were evaluated, all of which failed to perform satisfactorily. In response, TUV set up a certification system through which the minimum requirements which could be met by the available instruments were established and then were used as the basis for approval of devices. This is accomplished through 3 to 6 months of testing for each instrument, and was originally done for opacity monitoring systems, which are effective at PM loadings down to the 50 mg/m^3 level over a 3 m path length. In 1968 two instruments were approved. In 1972 light scattering devices were first tried, but the results were no better than with opacity monitors. By 1983, however, light scattering systems were approved for ambient monitoring, and by 1984, for stacks. Sigrist made the first PM CEMS based on light scattering. This device uses a heated isokinetic probe and sample line, and a heated optical cell where the light scattering measurement is made. This approach allows the system to handle droplets. A sampling rake can be used if single point sampling is not satisfactory. Later instruments developed by Sick and Durag make direct in-situ measurements, although for wet systems they can be configured like the Sigrist system. In 1986 continuous PM monitoring was required at PM levels too low for opacity monitors. Light scattering is orders of magnitude more

sensitive, however, and has become the method of choice for measuring low PM levels in Germany. Since 1986 TUV has approved 70 to 100 Sigrist systems, 200 to 300 Sick systems, and an unknown number of Durag systems.

Although a considerable amount of experience and data exists in connection with the TUV certifications and subsequent operations at various installations, this information is generally not available. TUV certifications are paid for by the CEMS manufacturer and are proprietary. CEMS operating data at facilities belongs to the individual facilities, and is also not public information. Since this data also represents the plant's emissions history they are reluctant to release it. For these reasons, TUV itself has no prepared reports on the general subject of PM CEMS performance. The only specific information that has been gathered to date comes from the TUV certification report for the Sick RM200 at a secondary lead smelter that Sick Optic-Electronic has made available to the EPA (discussed in the nest section).

The TUV certification process includes both laboratory and field testing. The laboratory portion of the testing is carried out to determine if various performance specifications are met during the basic operation of the instrument. The field portion of the testing is termed "suitability" testing, and is carried out to determine the performance of the CEMS in actual operational conditions. Some aspects of the performance specifications that are evaluated during the laboratory testing include the following.

1) Sensitivity of the instrument output to temperature in the range of -20 to 50 C should be less than 2% of full scale.

2) Sensitivity of the instrument output to supply voltage fluctuations of -15 to +10% should be less than 2% of full scale.

3) Response of the instrument to a set of internal calibration standards (ie, neutral density filters) should be within < 2% of the standard.

Items 1) and 2) are requirements that the instrument output not be biased by two specific environmental variables: ambient (outside) temperature and supply voltage. Item 3) is essentially a linearity check, and ensures that to within 4% all like instruments give the same response. It is important to note that this means that each instrument of a particular model and make is required to have the same response. That is, the instruments are interchangeable. Thus, if an instrument that is installed and calibrated in the field fails or suffers from a deterioration of performance, a replacement instrument can be installed and identical readings obtained without the need to recalibrate.

Suitability testing is carried out to assess whether or not performance specifications for reproducibility, drift, and accuracy can be met under actual field conditions, and to assess the long term endurance and maintenance requirements of the CEMS. Some of the performance specifications are:

1) Zero point drift of < 2% over the maintenance interval.

2) Sensitivity drift, as determined by an internal calibration, of < 2% over the maintenance interval.

3) Automatic corrections to the reference point to account for the build-up of dirt on the optics are limited to 6%. At that point an alarm must be given and the instrument serviced. The time that it takes to reach this situation determines the maintenance interval, and is a function of the effectiveness of the purge system.

4) Data availability during the suitability test must be greater than 95%.

Items 1) and 2) are analogous to the zero and calibration drift requirements required by the EPA in the performance specifications set forth in 40 CFR part 60, appendix B. Items 3) and 4) are analogous to the data quality assurance requirements for zero and calibration drift and data availability set forth in 40 CFR part 60, appendix F.

In general, satisfactory performance must be demonstrated at each kind of facility for which the CEMS maker wishes to provide instruments by carrying out a suitability test. During the suitability test 2 to 3 calibrations are made over the duration of the test, which lasts from 3 to 6 months (there should be a 3 month separation between calibrations). A statistical correlation between the CEMS measurement and the PM loading must be demonstrated. The regulations also require that scale and zero checks be performed at least once per maintenance interval, although they may be performed more frequently. The maintenance interval is determined by TUV during suitability testing, and should be at least one week.

A hierarchy of difficulty in terms of suitability testing exists: incinerators are most difficult, followed by coal, oil, and gas fired plants. Thus, if suitability is established for incinerators, the instrument is also approved for the other type of facilities. However, if suitability is established, for example, for an oil fired facility, then the instrument is approved for oil and gas fired facilities only, not for coal fired facilities or incinerators. Cement kilns are a separate, special class of facilities, as are other esoteric systems, such as metal recovery furnaces, for which suitability must be demonstrated without reference to other classes of facilities.

At each site that a monitor is installed, a calibration against the manual reference method must be performed. This calibration is checked every 3 to 5 years. The calibration is used to establish a linear correlation between the instrument response and the PM mass loading. The calibration relation is only considered valid for the range of PM loadings over which the calibration is performed, thus it is preferred to calibrate over a PM range spanning approximately one-half to two times the emission standard. Natural plant variability may provide sufficient variation in PM loading to obtain a calibration, however, if this is not the case, then higher emissions can be obtained by, for example, replacing a bag with a plate with a hole in it. A calibration is performed by making simultaneous manual measurements. 15 to 20 measurements are made (a minimum of nine is required) in a network that provides spatial coverage of the duct. Typically half-hour samples are obtained, and for comparison the CEMS measurements are integrated over the manual method sampling period. TUV performs the calibrations, which have been carried out for dust loadings as low as 50 $\mu g/m^3$ (0.00002 gr/dscf). The costs for a calibration range from about $7,000 for a small stack to about $18,000 for a large one.

Because PM CEMS based on light scattering are sensitive to changes in particle size distribution and composition, the stability of the calibration is of concern. It has generally been found that for plants with a high degree of flue gas clean-up, for example hazardous and municipal waste incinerators, which must meet or exceed 0.005 gr/dscf, that a stable calibration can be obtained. However, if changes are made to the plant, or to its operation (such as different fuel type), then the CEMS must be recalibrated. If a facility expects to burn different types of fuels at different times, it can calibrate for each fuel and use the appropriate calibration as required. At the periodic recalibration that is required, four comparison measurements with the reference method are made initially. If they fall within the error bounds of the original calibration then a recalibration is not needed. As an example, Mr. Buhne mentioned a calibration check performed after 5 years. The measurements were 15% different, but within the error of the original calibration, so the original calibration was considered to still be valid.

The regulations pertaining to the use of PM CEMS for compliance monitoring in Germany are summarized below. Continuous monitoring of PM emissions are required for hazardous and municipal waste incinerators, and all boilers with a thermal capacity greater than 5 MW. Emission limits are specified for never to exceed, half-hour averages, and daily averages. The daily average emission limit for MWC's is 10 mg/m^3 (about 0.005 gr/dscf) and for HWI's it is 1 mg/m^3.

Instrument availability is required to be >90%. It is further required that there be at least 20 minutes of valid measurements per half-hour averaging period. Once per day, all the results are transmitted by phone to the government. Any alarms (exceedances) are transmitted immediately. The measurement range of the instrument should be from 10% of the emission limit to 2.5 times

the emission limit (full scale). Upon installation, the CEMS must be calibrated against manual gravimetric measurements. Periodic recalibration is required at 3 to 5 year intervals depending on the type of facility. The uncertainty of the calibration relation, taken at the emission limit, gives the maximum measured value that is allowed (emission limit plus uncertainty). This value is determined for daily and hourly averages as well as for single data points. There is a required yearly linearity check, which is performed by TUV or an equivalent organization using calibrated filters . The German regulations pertaining to CEMS are compared to the EPA requirements as contained in 40 CFR part 60, appendices B and F in Table 2-4.

The German approach to the use of CEMS for compliance monitoring is based on the application of a practical engineering philosophy. CEMS are employed, despite the known sensitivities to various factors such as particle composition and size distribution, within the statistical limitations determined by a site specific calibration procedure that defines the statistical relationship between CEMS response and PM loading. The reliability of the CEMS and the statistical relationships are assured as best as possible through performance based CEMS specifications and suitability testing and other long term tests run on plants at normal operating conditions using both CEMS and manual methods. This allows the development of confidence in the utility of the CEMS.

The calibration of PM CEMS over a range of plant and APCD operating conditions allows a fit to a range of data that covers differing PM properties and size distributions. The resulting correlation will have larger uncertainty than one derived from changes to PM loading alone, but this is known and taken into account by the statistical treatment of the data. This is illustrated in Figures 2-1 and 2-2, which follow an example from Jahnke (1984). Figure 2-1 shows three hypothetical calibrations obtained for three different combinations of particle properties and size. For each individual type of particle, the calibration is obtained by varying loading only. The correlation (dashed line) for each calibration is very good. In practice, a calibration obtained by varying plant parameters might result in a set of data encompassing all of the points in Figure 2-1. The calibration that would be derived is shown in Figure 2-2 (dashed line), from which it can be seen that a much larger statistical uncertainty (bounded by the solid lines) is associated with the regression analysis. However, given this uncertainty, the relationship is still useful, and compliance can be based upon it.

2.1.13 Example of TUV Certification

The only documentation that EPA was able to obtain was provided by Sick Electro-Optic and described the TUV certification of the Sick RM200 light scattering based PM CEMS at a secondary lead smelter (TUV Rheinland, 1992). The laboratory phase of the testing was carried out

using the RM100 soot number detector, which is identical to the RM200 except for the available measurement ranges. Tests of sensitivity to changes in temperature and voltage, and response to standard calibration aids were passed satisfactorily

Duration, or suitability testing, was carried out downstream of the baghouse at a secondary lead smelter. Three RM200 units were installed in January of 1991 on a horizontal section of an 1 m diameter duct. The units were calibrated against duplicate reference method measurements on 4/15 & 16 of 1991. In the interim, the linearity of the units was checked (the units passed as the results were within 2% of the standards). During the January to April time period problems with the operation of one of the units were encountered due to a loose screw, and the same unit also exhibited some sort of temperature sensitivity (which was never fully diagnosed and which eventually went away, but which should not have occurred at all). During the calibration, drift was observed due to temperature sensitivity and stray sunlight. In April and May dirt build-up on the optics due to problems with the purge system caused periodic episodes of continuous initiation of calibration cycles. There was also an instance of simultaneous initiation of calibration cycles by all three units due to voltage fluctuations.

A second calibration was carried out on 5/27 of 1991 and the units were inspected. It was found that the light traps were badly corroded, and one was filled with deposits. The optics on at least one of the units were found to be very dirty due to a faulty purge system. Subsequent repairs and minor changes to the purge system were not effective in keeping the optics clean. The operational consequence of dirty optics is that the instrument carries out frequent calibration cycles to correct for the problem. However, dirt accumulation leading to over 6% attenuation is considered to be automatically out of specification. On 6/7 a modified purge system was installed, but by 6/20 unit #3 was dirty again. A check of all the instruments made on 6/25 showed the following attenuations due to dirt build-up on the optics of each instrument: #1 3.4%, #2 7.5%, #3 14%. The units were cleaned, but by 6/28 #1 and #2 were heavily dirtied again and running repeated calibration cycles. By 7/1 unit #3 was dirty also. At this point TUV and Sick agreed to halt the testing and Sick started work on a redesign of the instrument, particularly the purge system.

On 9/6 testing was resumed with two new instruments, #4 and #5. By 9/16 #4 had evidence of dirt build-up, and as a result a part was changed. From 9/30 to 11/2 both units ran with no problems: there was some dirt build-up, but it was largely within limits and the systems produced valid measurements. A history of the attenuation checks is as follows: 10/2 - #4 6.1% (cleaned), #5 1.7%; 10/25 - #4 2.2%, #5 3.9%; 11/4 - #5 5.2%; 11/8 - #4 2.2%, #5 6.4%. On 9/30 and 10/2 units 4 and 5 were calibrated.

The results of the duration testing are summarized below.

a) Reproducibility: Units 1,2, and 3 from 3/13 - 6/5 FAILED. Units 4 and 5 from 9/6 to 11/8 PASSED.

b) Availability: (should be >95%). All units passed.

c) Calibrations: the measurement network used for the manual reference measurements confirmed the representativeness of the CEMS measurement points. The duplicate RM200 measurements were better at the end of the test period (new units #4 and #5) due to better rejection of stray light. A statistical correlation between the RM200 measurements and total PM was demonstrated. The correlation coefficient for data lumped together from all three calibrations was 0.891. The individual calibrations were found to have a relatively large uncertainty which was ascribed to the working of the kiln, which operates in cycles: charging, smelting, removal, slag melting and removal (which presumably gives rise to highly variable particulate properties). No attempt was made to assess the stability of the calibration using the data from the three calibrations.

The uncertainty in the calibration data described above is presumably worse than what might be seen at other types of plants for the reason given above (the uncertainty in the calibration cannot be explained as that due to the reference method, although the reference method does have higher uncertainty than the RM200 measurements). In the TUV analysis, all the calibrations are used together to demonstrate the existence of an acceptable correlation between the RM200 measurements and PM loading. It is stated that, in principle, this data can be used to show the stability of the calibration, but this was not done. The data from the three calibrations covers data from times when the instruments were having some difficulty due to the rapid build-up of dirt on the optics. The design of units 4 and 5 was also apparently changed to allow better rejection of background light. However, the use of all the data by TUV to make a master calibration seems to indicate that the data is, to at least some degree, directly comparable; therefore a comparison of the initial calibration to data taken during the later calibrations is carried out here. The data from the first calibration, along with the regression line and confidence and tolerance intervals are shown in Figure 2-3. Figure 2-4 shows the same regression analysis with data from the second and third calibrations overlaid. Within the rather large statistical uncertainty of the regression analysis of the first calibration, all of the data are consistent. There do appear to be some systematic variations in the data in that almost all of the second and third calibration series data lies below the regression line itself, but almost all of the data are within the tolerance interval of the first calibration. The master calibration based on all of the calibration data is shown in Figure 2-5 along with confidence

and tolerance intervals. The data points and regression line from this graph are shown again in Figure 2-6 in relation to the regression line, confidence interval, and tolerance interval of the initial calibration. Note that, although the master calibration regression analysis can be taken as the "true" relation between RM200 response and PM loading for this facility, within the confidence interval calculated from the first calibration series, the regression line for calibration series one is in agreement with the master calibration. One can conclude, then, that within the statistical uncertainty of the data, the calibration relation for the RM200 response and the PM loading remained constant over the duration of the suitability testing, a period of about 6 months.

The duplicate reference method measurements are shown in Figure 2-7 for the third calibration series, and the duplicate RM200 measurements are shown in Figure 2-8. The reproducibility of the RM200 measurements is excellent, and is considerably better than that for the reference measurements. For units 4 and 5, TUV determined that the reproducibility, defined as R = <X>/U, where <X> is the mean of the measurements from the two instruments and U is the uncertainty, was greater than 30, as required (this corresponds to a fractional error between duplicate measurements of 3.3% or less).

It should be noted that TUV approval testing is part of any development program for a CEMS in Germany and is used as a final test to verify that the performance objectives have been met. The Sick RM200 was the first instrument using an in-situ approach for light scattering monitors and the problems revealed during the suitability testing of instruments 1, 2, and 3 reflect this fact. Furthermore, these problems were related to the suitability of the design of the instrument for in-situ monitoring rather than to any fundamental questions concerning the stability of the calibration relation, which is a separate issue. Based on the results of the endurance testing described above, in particular the performance of the new units 4 and 5, the RM200 received TUV approval with a 4 week maintenance (optical cleaning) interval required.

The description of the TUV certification of the Sick RM200 at a secondary lead smelter illustrates the PM CEMS approval process. The initial performance of the device was unsatisfactory. However, the maker redesigned the instrument and testing was continued. The redesigned device passed the performance requirements and gained approval, with TUV specifying the maintenance interval based on the test results. The data from the certification test also demonstrated a good correlation between the RM200 response and PM loading. Analysis of the data shows that the calibration of the RM200 remained stable, within the statistical confidence interval of the linear regression to the data, over the 6 month duration of the testing.

2.1.14 Conclusions

A variety of devices capable of continuously monitoring PM emissions are currently commercially available. Of the approaches surveyed in this report, one is not suitable for stack monitoring (the TOEM), and opacity monitoring lacks the required sensitivity. Of the remaining approaches, none makes a direct measurement of particle mass concentration, although the beta gauge calibration depends so weakly on particulate properties that the calibration is considered universal and absolute (Wedding and Weigand, 1993). The other devices require a site specific calibration against manual gravimetric measurements. The accuracy that can be obtained in this manner is not known, as it depends on the stability of the calibration. This depends in turn on a stable relationship between the measured particle properties and particle mass. The best way to determine the feasibility of applying these devices as CEMS for compliance purposes is to conduct field trials at the various types of sources to be regulated. A demonstration of these devices at facilities representative of the various source categories should determine how actual variations in PM size and composition affect the accuracy of mass concentrations inferred from the measured properties. It should be noted that in Germany, light scattering has been deemed sufficiently reliable for this method to have received certification for use as a CEMS.

2.2 CEMS FOR MERCURY

2.2.1 Introduction

There are two classes of CEMS for mercury: those designed to measure total mercury emissions (elemental and speciated mercury) and those that measure gas-phase elemental mercury only. The latter are designed to make direct in-situ measurements using optical techniques. The former include CEMS based on a variety of different approaches, some of which can also measure PM bound mercury. All of these CEMS are extractive. The approaches taken to making total mercury measurements employ thermal, catalytic, or chemical processes to convert speciated mercury to elemental mercury followed by detection of elemental mercury by means of photometric techniques or solid state sensors. One approach does not use a converter but instead attempts to measure the different mercury species directly. Mercury CEMS, organized by these different types of technologies, are listed in Table 2-5. The CEMS makers and developers listed in this table comprise all of the potential CEMS that have been identified in this study. There may be developers pursuing other approaches or the same approaches identified here that were not contacted and listed in the table.

2.2.2 Verewa Total Mercury Monitor

The Verewa total mercury monitor uses a heated probe to isokinetically extract a continuous sample of stack gas. The sample then passes through several treatments before being

analyzed. The first treatment uses an IR oven to heat the sample to 800C, which vaporizes Hg on PM and destroys all organic compounds, which can cause interferences. The second treatment uses a sodium-hydroboron solution to reduce all mercury compounds to elemental Hg. Elemental mercury is then detected in the gas phase by a UV photometer. Calibration is achieved by introduction of a mercury solution upstream of the IR oven. The detection limit of the device is specified as less than 10 $\mu g/m^3$. The maintenance interval of the device is cited as being greater than one week, and the solutions used in the device need periodic replacing. The Verewa total mercury monitor is currently commercially available in the US and costs $130,000, although it has not been demonstrated in the US. It has TUV lab approval, and is currently undergoing field trials in Germany. About fifteen units are installed worldwide (Verewa, 1994).

Advantages:

- Only monitor commercially available for total Hg.
- Measures total Hg: elemental, speciated, and PM bound.

Disadvantages:

- Relatively complex flow system for chemical conversion of speciated mercury.
- Solutions need replenishment.

2.2.3 ADA Technologies Total Mercury Monitor

ADA Technologies is developing a total mercury monitor that will be capable of measuring both total mercury and elemental mercury concentrations. By taking the difference between these two measurements, the speciated mercury concentration can also be reported. The monitor makes these measurements by employing a thermal converter (which can be bypassed) and a patented UV absorption cell for detection of elemental mercury. The converter is designed to convert all speciated mercury to elemental mercury, and has been tested in the laboratory with mercuric chloride and methyl-mercury. The stack gases are sampled continuously and first passed through a particulate filter, so as currently designed the monitor does not measure PM bound mercury. Calibration is accomplished using two calibration sources: a permeation tube for elemental mercury which is used to calibrate the detector, and a diffusion vial for mercuric chloride, which is used to calibrate the converter. Detection limits for this device are specified as being less than 1 $\mu g/m^3$.

ADA currently has assembled and tested their first prototype instrument. It has been field tested at a plasma hearth waste treatment unit operated by SAIC in Idaho Falls, ID. Details of and

data from this testing are not available. ADA plans to have a commercial instrument by the end of 1995 produced in partnership with Land Combustion (Schlager et al., 1995 and ADA technologies Inc., 1995).

Advantages:

- < 1 $\mu g/m^3$ detection limit.
- Simple conversion of speciated to elemental mercury.
- Capability to report split between elemental and speciated mercury.
- Calibrates with both elemental mercury and mercuric chloride sources.

Disadvantages:

- Does not measure PM bound mercury.
- Not commercially available or extensively field tested.

2.2.4 Senova Total Mercury Monitor

Senova is developing a total mercury monitor that uses a catalytic converter to convert speciated mercury to elemental mercury and a solid state sensor to detect elemental mercury. No information is available on the performance of the converter, and calibration is accomplished with an elemental mercury permeation tube only. The detection limit of the monitor is specified as less than 1 $\mu g/m^3$. The stack gases are sampled continuously and first passed through a particulate filter, so as currently designed the monitor does not measure PM bound mercury.

A prototype of this monitor will be tested as part of the joint DOE/EPA CEMS demonstration to be conducted at the IRF in Jefferson, Arkansas in July through September of 1995. Senova expects to have a commercial instrument ready sometime in 1996. They currently have a phase II SBIR in place to develop a capability to measure PM bound mercury as well (Senova Corp., 1995).

Advantages:

- < 1 $\mu g/m^3$ detection limit.
- Simple conversion of speciated to elemental mercury.

Disadvantages:

- Does not measure PM bound mercury.
- Not commercially available or extensively field tested.

2.2.5 PSI Total Mercury Monitor

Physical Sciences Inc. (PSI) is developing a total mercury monitor based on dielectric barrier discharge technology and emission Spectroscopy for detection. This monitor uses dilution sampling to extract a continuous sample from the stack. The sampled gas then enters a dielectric barrier discharge. The discharge excites nitrogen (the predominant background gas), which in turn excites elemental mercury. The nitrogen also dissociates $HgCl_2$ to HgCl, which also emits light. A spectrometer can then be used to detect the emission from elemental mercury and HgCl at their respective characteristic wavelengths. To date, laboratory tests have demonstrated quantitative detection of elemental mercury and mercuric chloride ($HgCl_2$). Detection of PM bound mercury has also been demonstrated, but not on a quantitative basis. Detection of other speciated mercury compounds has not been demonstrated, and may be problematic, as each species must be spectroscopically detected on an individual basis in this approach. Detection limits for this monitor are estimated to be in less than 10 $\mu g/m^3$. Calibration is performed with mercury permeation tubes and mercuric chloride diffusion vials.

PSI currently has a prototype that they plan to begin field testing in the fall of 1995 under a phase II SBIR. They do not yet have an estimated time to market for this device, and it may not be suitable as a total mercury monitor (it may be marketed as an elemental mercury monitor only) (Physical Sciences Inc., 1995).

Advantages:

- May measure PM bound mercury.
- Makes direct measurement of elemental mercury and mercuric chloride (does not rely on a converter.

Disadvantages:

- May not measure all forms of speciated mercury.
- Not commercially available or extensively field tested.

2.2.6 ABB Opsis Elemental Mercury Monitor

The Opsis system makes in-situ (cross-stack) measurements using the optical measurement technique known as differential optical absorption Spectroscopy (DOAS). The principle is as follows. Many species absorb infrared, visible, and ultraviolet light. A broadband light source is projected through the gas sample to a detector, and species present in the sample absorb light from

the beam at characteristic wavelengths. The measurement is made by using a spectrometer to look at both the specific spectral bands where absorption occurs and at reference wavelengths where no absorption occurs. The difference in the transmitted light at these wavelengths can be used to calculate concentration.

The Opsis system is a multicomponent analyzer. It can simultaneously detect some acid gases, NO_x, SO_x, water, and many organics (it operates at both IR and UV wavelengths), as well as elemental gas phase mercury. Different configurations can be purchased which will detect different combinations of these pollutants, including one version that measures mercury only. However, the single component system for mercury costs $120,000, while the multicomponent system only costs $150,000. Detection limits depend on the measurement path length: for a 5 meter path, the detection limit for elemental mercury is 2 $\mu g/m^3$ (10 $\mu g/m^3$ for a one meter path). Opsis is TUV approved in Germany, and there are over 100 units of all types installed worldwide. Opsis provides continuous measurement, and maintenance is low: about two hours per month, with three to four days of initial training (ABB Power Plant Controls, 1995 and TUV Rheinland, 1995).

Advantages:

- Multicomponent measurements.
- In-situ.
- Commercially available and TUV certified.

Disadvantages:

- Elemental mercury only.

2.2.7 Summary

The various total mercury monitors under development differ in whether or not PM bound mercury is detected, whether or not the converter is bypassed to give a separate measurement of total and elemental mercury, and in details of calibration. However, all of these monitors could be easily modified to allow measurement of PM bound mercury by addition of an oven, to allow separate measurement of total and elemental mercury by addition of a bypass around the converter, and to calibrate with both elemental mercury and mercuric chloride by the addition of another calibration source. Thus several technologies for the measurement of total mercury appear to be feasible and will be available soon. The PSI mercury CEMS is probably the furtherest from market, and may be applicable to elemental, or to elemental plus mercuric chloride only. It may

thus find application only in certain situations. The Opsis system, while offering simplicity, and multi-component in-situ measurement capability, only measures elemental mercury. For mercury monitoring, it also may find application in only certain situations, such as downstream of wet scrubbers providing control of mercuric chloride.

2.2.8 Conclusion

A variety of mercury monitors are already available or under development with availability scheduled within the year. Three of these monitors will most likely be suitable for monitoring total mercury: elemental gas phase and PM bound mercury, and speciated mercury. In addition, at least one and possibly two monitors will be available for measuring elemental mercury only. All of these monitors will have detection limits below or substantially below the proposed mercury emission limit. Two of these monitors will have undergone testing by TUV in Germany. However, at this point little field testing has taken place in the US. A demonstration program with field testing of the CEMS against EPA reference methods will be required in this country in order to ensure the successful application of these monitors to emission monitoring for compliance on hazardous waste burning facilities.

2.3 CEMS FOR ACID GASES

2.3.1 Introduction

There is a broad range of different approaches to making measurements of acid gases (mainly HCl and Cl2). These include non-dispersive infrared (NDIR) Spectroscopy, ion-selective electrode (ISE) techniques, ion mobility Spectroscopy (IMS), ultraviolet (UV) Spectroscopy, colormetric techniques, Fourier Transform infrared (FTIR) Spectroscopy, and mass spectrometric techniques. Acid gas CEMS, organized by these different types of technologies, are listed in Table 2-6. Note that not all makers of CEMS of a given type were contacted (although in each case at least one was, in order to establish the capabilities and approximate cost of the technology), and that not all makers in each category are necessarily listed. The colormetric CEMS is not included in the discussion that follows because field tests have shown that it is not an appropriate technology for monitoring stack emission of HCl from hazardous waste incinerators (Shanklin et al., 1991).

2.3.2 NDIR Spectroscopy

The term "non-dispersive infrared (NDIR) Spectroscopy" actually covers a variety spectroscopic techniques. However, the four NDIR based HCl CEMS identified here utilize the

same approach, which is known as gas filter correlation (GFC). The GFC technique involves making a sequential measurement. First, a broadband infrared (IR) beam is passed through the gas sample to be analyzed. All species present in the gas sample that can absorb the IR beam do so, including the target species, in this case HCl. Second, a gas filter containing the target species is also placed in the beam. This removes light absorbed by only that species from the beam. The light then passes through the gas sample, where, as before, all species absorb some of the light. Thus the difference in the amount of light reaching the detector in these two cases is due solely to absorption by the target species. This technique is thus a powerful way to eliminate spectral interferences, and can be applied to making measurements of many different species.

Four CEMS for monitoring HCl using the GFC technique are commercially available. These are made by Bodenseewerk, TECO, Servomex, and AIM. Bodenseewerk and AIM also make multicomponent GFC analyzers for NO_x, SO_x, CO, CO_2, H_2O, CH_4, NH_3, and HCl. Bodenseewerk, Servomex, and AIM use hot/wet extractive sampling systems, while TECO uses a dilution sampler. As discussed in Section 2.4.9, a GFC based analyzer using hot/wet sampling has been shown to operate successfully on HWI's. AIM also makes versions of their CEMS employing cross-stack in-situ monitoring. Costs for the various systems are summarized in Table 2-6, and performance in Table 2-7. These types of systems typically have detection limits around 1 ppm, response times of under a minute, and are interference free. All four makers have numerous systems installed world-wide, Bodenseewerk is TUV approved in Germany, and Servomex has passed certification testing in the State of Maryland (Shanklin et al., 1991, Thermo Environmental Instruments Inc., 1994, Servomex Co., 1994, Air Instruments and Measurements Inc., 1994, and Joseph et al., 1993).

Advantages:

- Sensitivity to 1 ppm and below (longer path length cells can be used, which increase cost and response time).
- Interference free.
- Relatively inexpensive.
- Can be combined with a multi-component analyzer.

Disadvantages:

- Does not measure Cl_2.

2.3.3 Ion Selective Electrode

The ion selective electrode (ISE) approach is based on a potentiometric measurement using a Cl^- ion-selective electrode. Typically a hot/wet extractive sampling system is used to bring the stack gases into contact with a scrubbing solution. The solution is formulated to adsorb HCl from the gas phase and to ensure dissociation to produce Cl^- ions for detection. Early ISE HCl CEMS had interference problems from other halides present in the stack gases from HWI's (see Section 2.4.9), however, at least two of the makers (Tess-Comm and Bran & Luebbe) have reformulated their solutions to avoid these problems. Bran & Luebbe has 500 to 600 systems installed on stacks world-wide, with about 30% of those being HWI's. The Bran & Luebbe is TUV approved in Germany.

The ISE approach is characterized by very low detection limits: Bran & Luebbe cites 0.3 - 0.4 ppm and Tess-Comm 0.4 ppb. Routine calibration can be accomplished using NIST traceable liquid solutions, and the devices are equipped to allow a gas calibration for relative accuracy tests. Response times of the instruments are less than one minute. ISE HCl CEMS are not sensitive to Cl_2. HF can also be detected using this technique, but a separate analyzer is required (Tess-Comm Inc., 1994 and Bran and Luebbe Inc., 1994).

Advantages:

- Excellent sensitivity: sub ppm.
- Relatively inexpensive.

Disadvantages:

- Does not measure Cl_2.
- Requires replenishment of scrubber solution.

2.3.4 Ion Mobility Spectroscopy

IMS systems are made for a wide variety of compounds and groups of compounds. In general, a separate analyzer is required in each case. Specificity is achieved in an IMS system through several different processes. First, a dilution sampling system is used to present a sample of stack gas to one side of a semi-permeable membrane. The membrane allows the species of interest to pass into the sample cell while rejecting or attenuating possible interferants. Next, the sample is ionized by a weak plasma generated by beta radiation from a radioactive source. A dopant may be added at this stage to increase ionization of the target species and thus further enhance specificity. The ionized sample is allowed periodically to enter a drift tube where the ions are propelled toward a detector by an electric field. As they cross the drift tube they are separated

on the basis of charge, mass, and shape. The time-dependent current generated by the detector constitutes a spectrum which is analyzed by a microprocessor to determine concentration based on peak height.

ETG makes IMS systems for HCl and Cl_2, HF and F_2, HBr and Br_2, I_2, and Cl_2O. Note that the HCl monitor is sensitive to Cl_2 as an interferant. The use of two analyzers with different ratios of HCl to Cl2 sensitivities could in principle be used to measure determine both HCl and Cl2 concentrations. This approach has never been attempted or demonstrated, however. The ETG IMS CEMS have sub-ppm sensitivity to HCl and HF with response times on the order of 30 seconds. ETG HCl IMS CEMS are installed on some stacks, mostly outside of the US (Bacon and Reategui, 1993 and Environmental Technologies Group, Inc., 1994).

Advantages:

- Excellent sensitivity: sub ppm.
- Measures total chlorine in both HCl and Cl_2.
- Relatively inexpensive.

Disadvantages:

- Can not distinguish between HCl and Cl_2.

2.3.5 Differential Optical Absorption Spectroscopy (DOAS)

The DOAS technique described previously in Section 3.2.6 for mercury monitors can also be applied to the measurement of Cl_2 using ultraviolet light and HCl using infrared light. ABB makes a system called Opsis based on this approach that is a multicomponent analyzer. It can simultaneously detect HCl and Cl_2, Cl_2O, and HF (as well as Hg, N_xO, S_xO, water, and many organics). Opsis is designed for open path measurements and for cross stack monitoring. Detection limits depend on the measurement path length: for a 20 foot path, the detection limit for Cl_2 is about 4 ppm, and for HCl it is sub-ppm. Opsis is TUV approved in Germany (ABB Power Plant Controls, 1995).

Advantages:

- Good sensitivity to HCl, Cl_2, and HF.
- Multicomponent measurements.
- In-situ.

Disadvantages:

- Relatively expensive.

2.3.6 FTIR

Fourier transform infrared (FTIR) Spectroscopy is an alternative technology to NDIR for measuring species concentrations based on infrared absorption that is capable of making simultaneous multiple species measurements. FTIR uses a broadband IR light source that is passed through the sample gas. The light then passes through a scanning Michelson interferometer, which rapidly samples a wide region of the IR spectrum. The resultant interferogram is recorded as the time dependent signal from a detector. A spectrum is recovered by Fourier transforming the detector output. The spectrum is then compared to reference spectra to identify species and make quantitative concentration measurements. The Fourier transform and comparison processes require a computer and sophisticated software.

FTIR spectrometers are available from quite a large number of makers for both open path measurements and for stack sampling. Stack sampling configurations use extractive probes and multipass absorption cells. For HCl, the sampling system and cell must be heated. Several FTIR makers provide such systems. These systems are typically capable of measuring CO, NO_x, SO_x, H_2O, NH_3, CH_4, HCl, HF, and HBr down to the 1 ppm level. Water vapor and CO_2 can both pose problems as interferants. Background from these two species can be handled by subtracting the appropriate reference spectra, and, in the case of water, by attempting to dry the sample. However, the presence of this background is often the limiting factor in making FTIR measurements.

FTIR CEMS are in routine use at a variety of different types of facilities for CO, CO_2, NO_x, SO_x, and VOC monitoring. FTIR systems for making HCl measurements are installed at a number of sites as demonstration systems (KVB, 1994, Enviroplan, 1994, Vidrine and McIntosh, 1993, Plummer et al., 1993).

Advantages:

- Good sensitivity: to the ppm level.
- Multicomponent analysis
- Can measure HF and HBr in addition to HCl.

Disadvantages:

- Can not measure Cl_2.
- Moderately expensive

• Ability to correct for water vapor interference is limiting factor for performance

2.3.7 Mass Spectrometry

Mass spectrometers operate by ionizing a gas sample in a vacuum chamber (by any one of several techniques, each with its own advantages). The species present in the gas are both ionized and fragmented. The ions then pass through a mass filter that separates them based on mass-to-charge ratio. The mass-to-charge ratio that is passed by the mass filter is continuously varied, thus generating a mass spectrum. Each species generates a distinctive spectrum, and can thus be identified and quantitated.

Many companies market process mass-spectrometers, which are capable of detecting any and all of the acid gas species of interest as well as many other components. Mass spectrometers integrated with hot/wet sampling systems for acid gas measurement are not commercially available, however, a prototype system has been tested with satisfactory results (Bartman et al., 1994). Mass spectrometers are in general capable of sub-ppm sensitivity.

Advantages:

• Excellent sensitivity: sub-ppm.
• Multicomponent analysis
• Can measure all acid gases in addition to HCl.

Disadvantages:

• Expensive

2.3.8 Summary

The main characteristics of each type of acid gas CEMS are summarized in Table 2-7. NDIR, ISE, and IMS are marketed commercially for HCl monitoring, and many units are already installed worldwide. The UV system also has the capability to monitor HCl and Cl_2, although it is sold as a multicomponent monitor. Units are currently installed worldwide, some of which are monitoring HCl. FTIR is also a multicomponent CEMS with the ability to monitor HCl, however, only a few systems are installed on a demonstration basis. And finally, MS, also a multicomponent technique, is still in the demonstration phase.

2.3.9 Previous Field Studies

From 1986 through 1991 the Quality Assurance Division of EPA's AREAL contracted with Entropy Environmentalists, Inc., to carry out a series of field tests evaluating HCl CEMS. Test were carried out at three municipal waste combustors (MWC's) and at two hazardous waste incinerators (HWI's) (Shanklin et al., 1991, Shanklin et al., 1989, and Rollins et al., 1988). The testing at the HWI's revealed problems with the CEMS that were not found during testing at the MWC's. A second round of testing at a HWI was carried out in 1990 after the CEMS makers had a chance to correct the shortcomings of the devices. A summary of the testing and the results follows below.

Initial tests were performed at MWC's with the following CEMS:

1) TECO Model 15 (NDIR gas filter correlation device with dilution probe).
2) Bodenseewerk Spectran (NDIR gas filter correlation device with heated sampling system).
3) Bran & Luebbe Ecometer (ISE with heated sampling system).
4) MDA Scientific Series 7100 (Colormetric, no sampling system).

The MDA colormetric system did not respond to HCl in the effluent sample, although it did respond to calibration gases. This system was dropped from further testing. At MWC's that did not control HCl emissions, the other three CEMS operated successfully. Test at MWC's that did control HCl emissions were inconclusive because the emission levels were very low (1 - 10 ppm), which made relative accuracy difficult to assess (there was also some concern over the accuracy of the calibration standard at these levels).

The first round of testing at an HWI in 1989 was conducted at the Trade Waste Incineration (TWI) facility in Sauget, IL. The CEMS tested were:

1) TECO Model 15 (NDIR gas filter correlation device with dilution probe).
2) Bodenseewerk Spectran (NDIR gas filter correlation device with heated sampling system).
3) Bran & Luebbe Ecometer (ISE with heated sampling system).

The results from the tests were inconclusive because: 1) the TECO dilution probe plugged; 2) the Bran & Luebbe electrode was fouled by a reaction with iodide; and 3) the Bodenseewerk Spectran was not set-up properly for the stack gas H_2O levels that were encountered. A second round of testing in 1990 was also conducted at the Trade Waste Incineration (TWI) facility in Sauget, IL after steps has been taken to correct each one of these problems. The CEMS tested were:

1) TECO Model 15 (NDIR gas filter correlation device with dilution probe).
2) Bodenseewerk Mekos 100 (NDIR gas filter correlation device with heated sampling system).
3) Bran & Luebbe Ecometer (ISE with heated sampling system).
4) Kyoto Model HL-26-11N (ISE with heated sampling system).
5) Tess-Comm Model 745 (ISE with heated sampling system).

The results of the performance evaluation were the following:

1) The ISE based CEMS were not reliable due to interference problems (the fix for the Bran & Luebbe CEMS was not successful).
2) The TECO system, which had earlier suffered from probe plugging problems, was operated successfully by heating the sampling system to a temperature 30F higher than the stack gas temperature. However, reliable operation was not achieved. It was thought that use of a dilution probe resulted in HCl levels at the analyzer that were too low to measure reproducibly.
3) The Bodenseewerk Mekos operated reliably.

A third round of testing was held in 1991 at a different HWI downstream of a wet scrubber. The CEMS tested were:

1) Tess-Comm (to asses whether they had fixed the interference problem).
2) TECO Model 15 (with a Perma-Pure drier in the sampling system rather than using a dilution system).

The results were the following:

1) The Tess-Comm operated successfully. The interference problem appears to be fixed.
2) The sampling system for the TECO system did not perform adequately.

In summary, one ion selective electrode system (Tess-Comm) and one NDIR system (Bodenseewerk) were shown to operate successfully at a hazardous waste incinerator. The TECO system, which does not utilize heated components, was unable to handle conditions characterized by less than 100 ppm HCl and greater than 20% H2O. The other ion selective electrode systems tested did not operate successfully at the HWI, although they may have been improved since the 1990 test, as the Tess-Comm was.

2.3.10 Conclusions

A large number of CEMS for HCl monitoring, encompassing a variety of different technologies, are currently commercially available. These include devices based on NDIR, ISE, IMS, and UV Spectroscopy. In addition, CEMS based on FTIR are available, although not in widespread use. Finally, the adaption of process mass spectrometers to HCl CEMS application has been demonstrated. Of these system types, NDIR and ISE have been evaluated at a HWI by the EPA (in 1990 - 91), and satisfactory performance was demonstrated. Since then systems based on IMS and UV Spectroscopy have become available and have been put into service. Systems based on NDIR, ISE, and UV Spectroscopy have been approved by TUV in Germany.

In conclusion, a variety of CEMS are available for immediate service monitoring compliance with HCl emission standards. Several of these CEMS are also capable of measuring other acid gases, either through the use of a second system (ISE, IMS), or simultaneously with a single instrument (DOAS, FTIR, MS). Cl_2 emissions can be monitored by UV DOAS or mass spectrometry (although this has not been demonstrated in the field).

2.4 CEMS FOR MULTI-METALS

2.4.1 Introduction

Current measurements of toxic metals are made using EPA Draft Method 29. Method 29 involves sampling the stack flow and collecting particle phase metals on a filter and volatile metals in a series of liquid filled impingers. The filters and impinger solutions are then sent to an analytical chemistry lab. The filter samples are digested in acid, and both the filter and impinger solutions are typically analyzed by inductively coupled plasma atomic emission Spectroscopy (ICP-AES). This procedure is capable of detecting all of the toxic metals of interest. In fact, the stack gas detection limits are determined by the volume of stack gas sampled. Since the sampling rate is chosen to ensure isokinetic sampling conditions, the sample volume is determined by the length of time that the stack gas is sampled. Typical samples are 1 to 5 m^3 and take several hours to collect. There are several limitations associated with Method 29. It is a manual technique for which continuous sampling is not practical. In addition, sending the samples to an analytical laboratory for analysis is time consuming and expensive. Thus Method 29 is not suitable for use as a CEMS, a purpose for which it was never intended.

The desired attributes of a metals CEMS are: continuous sampling of emissions, as close to real-time reporting as is practical, and automated, low-cost operation. In addition, detection limits must be low enough to assure compliance with regulatory limits. In this section five CEMS

under development are described.. These CEMS (listed in Table 2-8) are known as 3M (developed for use monitoring emissions from 3M's hazardous waste incinerator), HEST (Hazardous Element Sampling Train, under development by Chester Environmental), SPICAP (under development by Midwest Research Institute), on-line ICP (three different development efforts under way), and LASS (Laser Spark Spectroscopy, under development by Sandia-Livermore). The 3M CEMS is a semi-continuous method: sampling is continuous but averaged over long time periods, and analysis is on a batch basis using Method 29 techniques. The HEST CEMS collects a sample on filters which are analyzed by X-ray fluorescence (XRF) Spectroscopy. SPICAP collects the sample continuously in a liquid scrubber, and analysis is performed by standard ICP techniques. In the on-line ICP approach, the sampled stack gases are injected directly into an ICP for analysis. And finally, in LASS a laser is used to create a plasma directly in the stack gas, and the resultant atomic emission is used to analyze the metals concentrations. It should be noted that the analysis and discussion that follow are not based on a comprehensive literature search or industry survey. In fact, in certain cases, developers of CEMS technology are reluctant to make their efforts known or to release any detailed information.

2.4.2 3M

The 3M metals emission monitor is a "semi-continuous" technique that employs batch sampling to provide time averaged measurements (MRI, 1993). The sampling is performed at a single point and is subisokinetic (since particles at the 3M incinerator are primarily less than 2.5 microns). Particles are captured on a quartz filter and metals analysis is performed in the same manner as in Method 29. The volatile fraction is collected on a carbon impregnated filter (CIF) rather than the series of impingers used in Method 29. Once the volatile sample is digested, analysis is by the same methods as Method 29. The use of a CIF to capture volatile metals is a potential improvement over Method 29, as this eliminates the considerable complexity of using multiple impingers. 3M proposes to sample continuously, with the filters changed manually at fixed intervals (a sample interval of 4 hours was used in the preliminary tests described below) and sent to a laboratory for digestion and analysis. Thus the 3M method is a manual method with several simplifications over Method 29 to allow continuous sampling.

The 3M metals emissions monitor is being developed (by 3M, with assistance from MRI) to provide continuous sampling of the stack emissions from the 3M hazardous waste incinerator for compliance monitoring purposes. A preliminary validation test has been carried out in order to evaluate the essential features of the 3M method through comparison with Method 29. These features are:

- Single point sampling at a location in the fan breeching rather than high on the stack.
- The use of subisokinetic sampling in a situation where 80% of the particles are less than 2.5 microns.
- The use of carbon impregnated filters (CIFs) for volatile metals sampling.

The results of the preliminary tests are described below. They have importance ranging beyond the validation of the 3M approach in that they address several issues associated with features that the 3M method has in common with other proposed CEMS, such as single point probe sampling and the use of CIFs.

- Mercury concentrations measured through the use of CIFs were about 10 times those measured by standard Method 29 procedures. The reason for this discrepancy is unknown at this time.

- The use of single point sampling in the fan breeching was evaluated by carrying out a Method 301 comparison between the 3M method and Method 29. The results of the comparison revealed equivalent precision and slight bias high for some of the metals, particularly Cd, Cr, and Pb. Significant amounts of these three metals were also found in the probe wash (up to 40% for Cr), which was attributed to the association of these metals with larger particles (that accumulate in the probe). The association of these metals with larger particles would also explain the biasing high of the results for these metals, since subisokinetic sampling will tend to over sample large particles relative to small ones.

Thus the preliminary testing indicates that:

- Single point sampling is valid in this case.

- Subisokinetic sampling may be acceptable in this case (but is certainly not generally applicable).

- A significant fraction of the sample for some metals accumulates in the probe. A probe rinse therefore appears to be necessary for quantitative metals sampling.

In addition, a critical technical issue that still needs to be resolved is the use of the CIF's. The performance of CIFs are a function of temperature, chlorine concentration, oxygen concentration, sulfur concentration, and other factors. Therefore the range of conditions over which use of CIFs is appropriate needs to be determined.

In summary, the proposed 3M CEMS consists of a simplified sampling methodology (relative to Method 29) to allow continuous sampling of stack emissions. It is a manual method, with the filters changed by hand and sent to an analytical laboratory for Method 29 type analysis. The results of the analysis are therefore not immediately available, and in order to avoid large labor costs, the sampling interval must be long (otherwise too many samples are generated for analysis). Thus, it is not a continuous monitor in the sense implied by the term "CEMS." In fact, this approach suffers from the main limitation of Method 29: the analysis is a complex, time consuming, and costly procedure. Assuming a sampling interval of 24 hours and a per sample analysis cost of $500, the yearly cost for sample analysis alone is $360,000 (a particulate filter and a CIF are generated for analysis each sample period). On the other hand, the only equipment required is the simplified sampling system, thus initial installation costs will be low. It should be noted, however, that this approach may have utility in providing interim compliance monitoring on a time averaged basis until other CEMS are developed. The advantages and disadvantages of this approach are summarized below.

Advantages:

- Only a simple sampling system is required, therefore initial installation costs will be low.
- Established analysis procedures are already developed, therefore development costs will be low.

Disadvantages:

- Although sampling is continuous, averaging times are long and the analysis is not continuous.
- Analysis is complex, time consuming, and costly, with resultant reporting times on the order of weeks.

2.4.3 HEST

The HEST technique employs an isokinetic sampling system with quartz (teflon proposed) filter collection for particulates and CIFs for volatile metals (Cooper et al., 1992). The analysis of both filters is carried out by X-ray fluorescence spectrometry (XRF), which is capable of providing concentrations of all the desired toxic metals except beryllium (Be). In an automated HEST CEMS, a cassette or tape mechanism would remove the filters (replacing them with new ones) and possibly transport them to an on-site XRF spectrometer. The XRF analysis is carried out directly on the filters themselves and is non-destructive. Be analysis, if desired, must be carried out by

standard analytical techniques (Method 29).

XRF analysis is capable of potential detection limits (estimates based on detection limits measured to date and improvements that can be realized from optimization of the spectrometer and filter substrate) from roughly 1 to 50 times lower than those of Method 29 (one-twelfth the sample volume, and depending on the metal), with both sampling and analysis/reporting times on the order of tens of minutes (see Table 2-9, derived from data provided by Chester Environmental) (Cooper et al., 1993). In the absence of particle size effects, which are not expected to be important for sampling locations downstream of particulate control devices, calibration standards are available which offer accuracies of about 5%.

Chester Environmental (now part of TRC), the developer of HEST, has carried out preliminary testing of the components of a HEST CEMS. The HEST sampling train and off-site XRF analysis combination has been tested on the stack emissions from coal-fired power plants as part of the DOE flue gas clean-up program. Comparison between HEST and Method 29 measurements were made for As, Cd, Cr, Ni, Se, and Hg. The differences between the measurements by the two methods were not statistically significant except in the case of Ni (HEST measurements as much as 50% below the Method 29 values). Agreement was not good for 3 out of the 5 metals reported for one run in which very low metals concentrations were present. This was attributed to contamination of the Method 29 samples. No development of an optimized, integrated system with automated sampling and analysis has taken place, nor is such development planned at this time.

The advantages of the HEST technique are as follows. As in the case of the 3M technique, the use of impingers is eliminated. However, the HEST technique also eliminates the sample preparation process, since the filters can be analyzed directly by XRF. The sample handling and analysis is thus greatly simplified, reducing costs and chances for error. The samples may also be stored indefinitely for later reanalysis, if necessary. In addition, XRF analysis can be accomplished in minutes, the XRF device is compact, and stack detection limits are much better than those of Method 29 (for the same sample volume). The HEST technique can therefore provide on-site monitoring with potential sample integration and analysis times on the order of tens of minutes. The XRF technique itself is a well established analytical tool, and commercial systems are available. Chlorine and oxygen (from HCl and H_2O) are not expected to cause any analytical interferences.

The disadvantages of the HEST technique are the following. First, Be is not detectable by XRF, so if Be monitoring is desired, then part of the filter must be sent to an analytical lab for analysis by standard procedures. Second, XRF analysis cannot be employed in situations where

the particle loading on the filter is not uniform. Such a condition must be recognized and the filter analyzed by standard methods. There are also some interference problems between elements, such as between Ni and Co. Finally, the presence of sulfuric acid can cause physical breakdown of the filters and may also block the adsorption of mercury. Thus more study is required to determine the range of conditions over which mercury capture by CIF is quantitative. Demonstration of quantitative particulate capture meeting Method 5 standards using teflon filters will also need to be demonstrated, and the temperature range over which these filters can be used needs to be determined.

Another potential issue of concern is the fact that XRF spectrometry is sensitive to particle size effects. The attenuation of the fluoresced X-rays as they pass out of the bulk particulate material is energy dependent. Since each element emits at characteristic energies, the attenuation of the signal from each element will be different. This effect can therefore bias the measurements low, and the amount of bias will be different for each element, being more severe the lighter the element and the larger the particles. Clearly, if the particles are small enough, this effect will not be significant, and the XRF analysis is straightforward. Chester Environmental estimates an 8% attenuation for Cr (the worst case among the 10 hazardous elements that can be detected with XRF) for 10 micron carbon and quartz, and 15 micron limestone particles. For this effect to be important, then, a significant fraction of the particles would need to be greater than 10 microns. Table 2-10 shows Chester Environmental's estimate of the attenuation for each metal for the case of 10 micron carbon and quartz, and 15 micron limestone particles.

In summary, the proposed HEST CEMS offers batch sampling and on-site analysis with a time resolution on the order of 30 minutes and with detection limits superior to those of Method 29. Issues of concern are: 1) quantitative sampling due to accumulation of sample in the probe (how can a probe rinse, if needed, be incorporated), and 2) the range performance of the teflon and carbon impregnated filters. It is estimated that development of such a system, including prototype assembly and field demonstration, could take place in about 18 months at a cost of approximately $525,000.

Advantages:

- Non-destructive analysis, archivable samples.
- Well established analytical technique (XRF).
- Detection limits generally 10-100 times lower than Method 29 for equivalent sample volumes.

Disadvantages:

- Be is not detectable by XRF.
- Batch sampling/analysis and mechanical sample handling system.
- Reporting times on the order of tens of minutes.

2.4.4 SPICAP

SPICAP is a CEMS developed by MRI for other sensing applications that concentrates the particulate and vapor phase metals into a liquid stream by passing an isokinetically sampled gas stream from the stack through a proprietary liquid scrubber. The liquid containing the sample is then nebulized to generate an aerosol that is entrained into an ICP. Analysis is thus performed by standard liquid sample ICP techniques, although this procedure differs from Method 29 techniques in that the aerosol contains undigested particulates. The extent of the concentration that occurs in transferring the sample from the gas to liquid phase is determined by the ratio of the gas flow rate to the liquid flow rate. As currently proposed by MRI, SPICAP would have detection limits between 1 and 100 times lower than those of Method 29. SPICAP accomplishes this by using sampling rates about 100 times larger than those typically used by Method 29 (300L/min vs. 20L/min) with liquid withdrawal rates of 1 to 10 ml/min. The use of comparable sampling rates and liquid sample sizes in Method 29 would result in detection limits which are the same as those in the proposed SPICAP system. Response time of the SPICAP system is determined by the rate at which scrubber solution is removed (and replaced) and the total liquid volume in the system. Thus there is a trade off between response time and detection limits. Withdrawing solution at a rate of 10 ml/min, with a liquid volume of 150 ml would result in a time constant of about 15 minutes (MRI, 1993a).

SPICAP for use as a metals CEMS is currently at the conceptual stage. However, MRI has built working devices for other applications and is currently developing a system for hexavalent chromium monitoring. Testing of the Cr^{+6} sampling system has revealed the need for probe rinsing and a saturation tower (to prevent evaporation of scrubbing fluid), which increases the liquid volume in the system, and thus the response time. Based on this experience, MRI plans to incorporate a probe rinse in the proposed metals CEMS. To date, MRI has no external support for the development of SPICAP for use as a metals CEMS.

The essential feature of SPICAP is its ability to concentrate the gas phase sample into a liquid stream on a continuous basis. This confers the following advantages. Sample handling and introduction into the analysis instrument is inherently continuous and automatic and is accomplished by a liquid flow system. This feature lends itself to incorporating a continuous probe wash if sample accumulation in the probe is a problem (the wash liquid is simply combined with the rest of the sample in the scrubber). In addition, calibration of the analysis system is easily accomplished by switching from the scrubber to a series of standard calibration solutions

(this does not calibrate the sampling efficiency). In fact, an internal standard for monitoring system performance can be realized by doping the feed liquid with a metal not found in the stack emissions. Finally, a standard analytical ICP system is used for analysis, eliminating the need for development of the detection/analysis components of the CEMS.

The liquid sample handling feature also has disadvantages. Volatile metals other than mercury are captured with a nitric acid solution. If this solution is unsatisfactory for mercury capture, then use of a second scrubber containing a permanganate solution will be required. However, the scrubbers can be arranged in series and the mercury analysis carried out by UV absorption, and thus the additional cost is not great. In addition, the liquid scrubbers have relatively low capture efficiencies (ranging from 50 to 90%) which are dependent on particle size. In order to assure complete and consistent sampling, several scrubbers in series may be needed; this will increase the total fluid volume and hence the response time.

There are several issues that need to be addressed in the development of SPICAP. First. the behavior of particulates in the liquid handling system is an unknown and a source of potential problems. Difficulties may exist with the introduction of the particulate containing sample into the ICP and also with the dropout of particles in the flow system and later re-entrainment, leading to memory effects (hysteresis). In addition, incomplete volatilization of particles by the ICP will result in a bias of the measurement towards low values. If particulates prove to be a problem due to any of these effects, MRI proposes to use a continuous microwave digestion system in order to eliminate the particles. Second, the efficiency of particulate and volatile metals capture by the liquid scrubber will also need to be investigated. The particle capture efficiency is known to be dependent on size (less efficient for smaller particles), and both particulate and volatile capture efficiencies may be as low as 50%. One possible solution is to cascade a series of scrubbers, with the scrubbing solution feeding from one unit into the next. A high and consistent sampling efficiency would need to be demonstrated for the calibration to have validity. Finally, the issue of probe accumulation needs to be investigated and incorporation of a continuous probe rinse demonstrated. One possible solution may be to place a scrubber in the probe near the nozzle to capture large particles before they collect on the walls of the probe.

In summary, the proposed SPICAP CEMS offers continuous sampling and on-site analysis with a time resolution on the order of tens of minutes and with detection limits slightly lower than those of Method 29 owing to the high proposed sampling rate of several hundred liters per minute. The technical risks are few: engineering fixes to the problems of sampling efficiency and particle transport are available at the cost of added complexity. It is estimated that development of the SPICAP system, including prototype assembly and field demonstration, would take 15 months at a cost of $340,000.

Advantages:

- Continuous sampling and transport to the analytical device.
- Probe rinse easily accommodated.
- Well-established analytical technique (standard analytical ICP).
- Detection limits comparable to Method 29 for equal sample volumes.

Disadvantages:

- Separate system required for mercury.
- Response times on the order of tens of minutes.

2.4.5 On-Line ICP

On-line ICP refers to the continuous introduction of a gas sample directly into an ICP. Analysis by AES is then carried out in exactly the same manner as by conventional ICP. ICP analysis is capable of detecting all of the toxic metals of interest. The essential feature of on-line ICP is that it provides truly continuous monitoring (temporal resolution on the time scale of seconds or minutes). Estimated detection limits (based on the results for Ba, Cu, and Sr in the flue gas of a hazardous waste incinerator) derived from the work at China Lake are about a factor of three lower than those for Method 29 (2.5 m^3 sample) for most metals, with the exception of mercury (about two times higher) (Seltzer, 1993). Work at DOE Morgantown, sampling in a coal gasifier, has currently attained detection limits for various hazardous metals that are from 10 to 100 times higher than those for Method 29 (2.5 m^3 sample) (Meyer, 1993).

There are several efforts at on-line ICP CEMS development currently under way, including programs at DOD China Lake, DOE Morgantown, and ADA Technologies, Inc. (under DOE contract). A fourth program at Battelle Memorial Institute in Columbus, OH has been discontinued. Several different approaches for introducing the gas stream into the ICP subject to the flow constraints imposed by isokinetic sampling requirements and ICP input flow rate limitations have been developed and demonstrated, and quantitative measurements of more than a dozen different metals have been demonstrated.

The Naval Air Warfare Center (NAWC) at China Lake, California, has developed and demonstrated an on-line ICP for the measurement of Cu, Ba, and Sr in the flue gas of an incinerator burning pyrotechnic materials. This work used a commercially available air ICP. Such units currently operate at sample gas flow rates of about 1 L/min (total flow rate is 10 to 15 L/min), therefore requiring a sampling interface since the stack gas is sampled isokinetically at 10-20 L/min. The sample interface consisted of an injection loop that is filled at stack sampling rates and then emptied into the ICP at a lower rate. This scheme thus operates in a batch mode, with

samples being injected into the ICP 2-3 times a minute. Calibration is accomplished in the laboratory through comparison of signals generated by the introduction of standard aqueous solutions of metals and powders containing known metals concentrations. Field calibration can then be carried out using the standard solutions alone. Measured concentrations of Cu, Ba, and Sr in the incinerator flue gas were on the order of 1000 micrograms per cubic meter and were within a factor of three of concentrations determined by Method 29 sampling. The discrepancy may be due in part to different normalizations of the two data sets and to sample loss in the transfer line from the stack to the ICP (a 50 ft. heated line was used), and is currently being investigated. The efficiency of sample transport to the ICP needs further investigation, and clearly the configuration can be modified to reduce losses. A follow-on effort to develop a CEMS for multi-metals measurement has been funded by the US Army. In this effort, an argon ICP will be used rather than the air ICP employed to date due to the fact that effective excitation temperatures are higher in an Ar fueled ICP, and interference and background due to molecular species are reduced, thus resulting in better sensitivity. Air ICPs are better at volatilizing particles, however, there is a trade off in performance involved. The main tasks that need to be accomplished are: 1) optimization of the plasma operation and emission detection to maximize sensitivity (the metals studied thus far have relatively good signal to noise ratios), 2) characterization and optimization of the sampling interface, and 3) characterization of biases due to possible matrix effects (background from molecular gases due to variable amounts of C containing species, and the presence of N_2, NO, and OH emission, and particle distribution and loading effects). Estimated detection limits are shown in Table 2-11. A prototype CEMS using the new ICP will be installed in a trailer and field tested at the US Army munitions incinerator at Tooele, UT in the spring of 1996.

ADA Technologies in Denver, Colorado, is pursing development of an on-line ICP funded both internally and by an SBIR from DOE Morgantown (Hyatt et al., 1993). Phase I of the SBIR is nearing completion. In the Phase I work, simulated flue gas mixed with 90% argon is excited in an inductively coupled plasma. The ADA system requires dilution of the waste stream with argon to ensure a plasma that is sufficiently hot to vaporize and excite emission from all metals of interest. The metals emission must be detected in the presence of a strong background consisting mainly of NO and OH (A-X) band emission. Using background subtraction techniques, ADA demonstrated detection of Ti, Mg, Si, Al, V, Zn, Na, Fe, Pb, Cr, Mn, and Ba directly as constituents of fly ash and Cd, Se, and Hg in simulated flue gas (Hg and Se simultaneously at 100 ppm levels). Quantitative results have not yet been obtained. ADA plans to develop a field deployable device in Phase II for testing with actual stack gases. ADA is already actively exploring commercialization possibilities with instrument makers.

An in-house program at the Morgantown Energy Technology Center, Morgantown, West Virginia, has developed an on-line ICP for use in analyzing coal-fired gasification and combustion streams (Chisolm, 1993). This system utilizes an He-Ar ICP torch and a sampling interface that allows introduction of low flow rate sample gas to be introduced to the ICP. The sampling system

is heated, and the ICP is located at the sample point, with the electronics remotely located. Detection limits are sub ppm for some metals, although there may be problems with Pb and As. Particle size effects may also be a problem. The sample transport efficiency must also be studied to assure that there are no particle dropout problems. Gas phase detection limits available to date are listed in Table 2-12.

In summary, the various proposals for on-line ICP metals CEMS offer continuous sampling with real time on-site analysis. Direct sampling and analysis of a gas stream has an advantage in that this is the simplest possible scheme for stack gas sampling, and thus potentially the most reliable. There are no mechanical transport, liquid transport, or wet chemistry considerations. The development efforts at China Lake and DOE Morgantown are the furtherest along: they both have prototypes in operation. However, data for the 11 HAPs metals in a stack stream similar to that of a hazardous waste burning facility are not available. Estimates of the performance of a system optimized for this application are difficult to make, as performance depends on the type of ICP and the characteristics of the flue gas. Based on the work at China Lake, detection limits roughly equivalent to Method 29 with a $2.5m^3$ sample (2 hours at 20 L/min) can be reasonably expected. The work at China Lake has also established a potential calibration protocol. This calibration will not take into account sampling losses. There are several issues of concern that need to be addressed in the development of on-line ICP. Particle drop-out and sample accumulation in flow system between the probe and ICP is potentially problematic. Also there are potential background and bias problems from molecular emission. This may cause problems as water vapor and organic concentrations, and particle loading and size distribution, change. Finally, complete volatilization of particles must be assured.

Advantages:

- Simple, continuous sampling.
- Real-time analysis on the order of minutes.

Disadvantages:

- Characterization of background and interferences is required, and the resultant detection limits are not known with certainty (and will depend on the characteristics of the stack gas).

2.4.6 Laser Spark Spectroscopy (LASS)

LASS is the only "in-situ" method among the five potential CEMS that have been identified. In LASS, a high energy pulsed laser is focused into the gas stream to be analyzed, and

gas at the focal volume is dissociated and ionized to form a transient plasma. Particles present in the focal volume are volatilized and also contribute to the plasma. Analysis is accomplished by detecting the atomic emission from the plasma. LASS is thus similar to ICP in that plasma emission is used for metal detection and quantification. However, the laser, rather than an ICP, is the plasma source, and the plasma is created in the gas stream with no need for sampling. LASS is capable of performing continuous monitoring with a time resolution on the order of minutes. Current laboratory detection limits are shown in Table 2-13.

LASS is being developed at Sandia National Laboratories in Livermore, CA (Flower et al., 1993 and Otteson et al., 1989). There are still several fundamental issues that are being researched, such as particle effects, background problems, and calibration procedures which need to be developed. In addition, systematic effects that may bias the measurements, such as quenching of the emission, need to be investigated. In a complementary effort, the EPA Office of Research and Development is supporting basic research into these areas at SRI, International in Menlo Park, CA (Dave Crosley's group). A prototype LASS system has been assembled at Sandia, and has made demonstration measurements at a pilot scale Joule melter at Clemson University (Flower et al., 1995). Measurements of Cd at the 4 $\mu g/m^3$ level, Mn at the 14 $\mu g/m^3$ level, and Pb at the 2000 $\mu g/m^3$ level were demonstrated, although the accuracy of the measurements was not assessed through independent measurement or other knowledge of the concentrations. The detection limits determined in the field were from two to four times higher than those determined in the laboratory and listed in Table 2-13. In an effort to facilitate bringing this technology to market, Sandia has licenced the LASS technology to a private company which will center its efforts on demonstrating a prototype instrument in the field.

Particle size distribution and loading has the potential to affect LASS measurements. Particles larger than a certain size will not be completely volatilized, which will result in a bias low. Composition of the particles will also be a factor in determining the maximum size that will be completely volatilized. Particle light scattering along the optical path is also a potential problem which may limit the range of conditions for which this approach would be applicable. Routine calibration of an in-situ method such as LASS, required since system performance can be degraded by misalignment (caused by vibration) and dirt (coating the windows and/or optics), is also a difficult issue. Also, detection limits are high due in part to the presence of a large background signal (emission from NO, N_2, and OH from water breakdown, as in the case with on-line ICP). How this background behaves as conditions change can affect performance. Finally, the mechanism of plasma generation in LASS is quite different from that in an ICP, which has been well characterized as an analytical excitation source. It is not known how changing stack conditions will affect the plasma generation and metal emission in LASS.

In summary, the proposed LASS CEMS offers in-situ continuous measurements with a time response on the order of minutes. There are several technical risks: particle effects are

largely unknown, background problems must be overcome, and a practical calibration procedure must be developed. The primary attraction of LASS lies in the fact that it is an in-situ technique. This is a major advantage in that questions concerning the efficiency of probe sampling and sample transport are thus eliminated. Calibration of the optical system on the stack will also be required, which is envisioned to involve removing the optics from the stack and interfacing them with a calibration apparatus that includes some type of aerosol generator. This procedure would provide an overall system calibration, but would be cumbersome. Current detection limits are 1 to 50 times higher than those for Method 29. In addition, difficulties associated with bias due to changing conditions, such as water concentration and particle size, are largely unexplored.

Advantages:

- In-situ: no probe or sample transport needs.
- Real-time analysis with response times on the order of minutes.

Disadvantages:

- Calibration: appropriate source needs to be developed, and procedure is likely to be cumbersome.
- Characterization of background and interferences is required, and the resultant detection limits are not known with certainty (and will depend on the characteristics of the stack gas). Current detection limits are higher than those of the other proposed CEMS.

2.4.7 Comparison of Metals CEMS

Current detection limits for the candidate CEMS are compared to Method 29 detection limits in the Table 2-14. Potential detection limits for all the candidate CEMS are compared to the average emission levels of three cement kilns during compliance testing and to BIF rule limits calculated assuming a dispersion coefficient of 0.3 and a stack flow rate of 60 m^3/s in Table 2-15.

Detection limits averaged over all metals for the various CEMS are shown graphically as a function of sampling time in the Figure 2-9. Detection limits for HEST and Method 29 (3M is the same as Method 29) are a function of sample time. Detection limits for SPICAP are a function of sample rate and liquid withdrawal rate, which affect response time. Detection limits for LASS and on-line ICP are not functions of time (collection of sufficient photons takes less than a minute). HEST and SPICAP have the best detection limits, while on-line ICP has potential detection limits equivalent to about a 100 minute Method 29 sample (at 20L/min). Current LASS detection limits are higher, although the goal that the developer hopes to obtain is < 100 $\mu g/m^3$ for all of the HAPs

metals.

The detailed discussions of the individual CEMS in the preceding sections are summarized in Tables 2-16 and 2-17. Initial cost is not included because all of the candidate CEMS are estimated to cost between $100,000 and $200,000 with the exception of the 3M technique, which would cost less than $25,000 (achieved at the expense of much higher operating costs). The terms low, moderate, and high in assessing operating and maintenance costs are relative only (no absolute dollar costs have been determined as there is no experience operating or maintaining these devices in a CEMS application).

2.4.8 Conclusions

Five potential metals CEMS have been identified and evaluated. The results of this evaluation are the following. There are four potential CEMS approaches at different stages of development (HEST, SPICAP, On-line ICP, and LASS), each of which offers a unique combination of advantages and disadvantages. It may be that each will be best suited to differing ranges of stack conditions, and that no one CEMS will be universally applicable. The fifth approach, 3M, is not a true CEMS. It is, rather, "semi-continuous," and may have utility in an interim role, as it has a substantial lead in development.

Two of the approaches, HEST and SPICAP, are based on established analytical techniques. Their development is thus a question of engineering and demonstrating workable prototypes, and establishing the range of conditions to which they can be applied. Since these approaches are extractive, their biggest challenge is in solving the probe accumulation problem. Both of these CEMS have measurement times that will probably be between ten minutes and an hour. HEST has undergone extensive component testing, however, there is currently no backing for the development of a CEMS. SPICAP is the only probe-based CEMS that can easily incorporate a probe wash, and thus side-step the potential probe accumulation problem. Issues to be addressed concern sampling efficiency and transport. The components of a SPICAP CEMS will be field test in the summer of 1995 at the joint DOE/EPA CEMS demonstration project conducted at the IRF in Jefferson, AR.

The other two approaches, On-line ICP and LASS, have great potential as real-time CEMS. However, both have substantial development work remaining to done. The great attraction of LASS is its potential to allow in-situ measurement (avoiding probe accumulation problems), however, this also poses difficult challenges to obtaining quantitative results. A prototype system for field demonstration work is now available, although quantitative results have not yet been obtained. On-line ICP offers the potential combination of real-time monitoring capability with good performance. Key issues to be addressed are: 1) probe accumulation and 2) quantitative

detection in real conditions. Several development efforts are underway, with the program at China Lake being probably the best funded. This effort is on schedule for field testing at an incinerator in the spring of 1996.

2.5 CEMS FOR ORGANIC COMPOUNDS

2.5.1 Introduction

Organic compounds are currently measured using SW-846-0039 (VOST) and SW-846-0010 (Semi-VOST) (EPA Method 18, general organics). These methods involve batch sampling, with organics capture by filter, condensation, adsorption, or simple storage of the gas volume sampled. Analysis is typically by GC/MS (following extraction from the sample medium if necessary). These methods are manual methods and involve time consuming analysis. A need therefore exists for organics measurement technology that is automatic and provides on-site, real-time analysis. There are several technologies that are currently commercially available or under development that have the potential to meet these needs. These technologies are summarized in Table 2-18, in which they are organized by type of approach: fast cycle gas-chromatograph (GC), direct sample mass spectrometry (MS), ion-mobility Spectroscopy (IMS), ultraviolet (UV) Spectroscopy, fourier transform infrared (FTIR) Spectroscopy, photoelectric detection for particulate bound PAH, and laser induce fluorescence (LIF) for vapor phase PAH. The detailed information under each heading in the table is intended to represent a sample of the development activity underway, not a comprehensive survey.

2.5.2 Fast Cycle GC

Continuous GC with detection by mass spectrometry, flame ionization (FID), electron capture (ECD), and flame photometry (FPD) are currently under development. With a MS for detection, such a system is capable of species resolution in two dimensions, GC transit time and mass spectrum, and thus provides the highest degree of species specificity. This approach is capable of simultaneous multiple species detection at detection levels two to three orders of magnitude below those of FTIR. Less expensive approaches rely on simpler detection systems, such as FID, ECD, and FPD. These systems rely on the GC to provide most of the specificity, and when a complex mix of species is analyzed, can only distinguish between types of compounds.

There are several efforts underway to develop fast cycle GC for real time stack gas analysis. For instance, the Army has developed an on-line GC system designed to measure chemical warfare agent concentrations using a FPD to detect chemiluminescence from the HPO radical (National Research Council, 1994). The system has suffered from too many false positives

and calibration difficulties. A review of the program has recommended development of a GC/MS based system. Also, an automated vapor sampling system coupled to a short capillary GC column that allows sampling times of less than a second and analysis times on the order of minutes has been developed by researchers at the University of Utah This system has used MS, FTIR, and IMS detection (Meuzlar et al., 1994).

Advantages:

- Sensitivity to the ppb level.
- Selective for at least classes of compounds. When coupled to an MS, can be highly selective and sensitive.

Disadvantages:

- Periodic introduction of sample into GC.

2.5.3 Direct Sample MS

Mass spectrometers are capable of multi-species measurements with excellent sensitivity. Groups at both Los Alamos National Labs and Oak Ridge are developing direct sample ion-trap MS. The Los Alamos group is using a direct membrane sampling technology developed at Purdue University. Such a system is capable of response times on the order of minutes with sub-ppb sensitivity (Wong et al., 1995). Other groups are developing mobile MS based instruments, but details are not known at this time. Eli EcoLogic Inc. is marketing a commercially available direct sample mass spectrometer system made by the Austrian firm of V&F (EcoLogic Inc., 1994). This system uses a quadrapole mass spectrometer and “chemical” ionization that results in minimal fragmentation. This results in easier interpretation of mass spectra and enhanced sensitivity. The latest model of this device offers sub ppb sensitivity. This device has been tested on incinerators in Europe, Canada, and the US, and is currently in use on a number of incinerators in Europe. The cost of the unit is approximately $200,000. A potentially significant advancement in MS technology is the development by Westinghouse of a mass spectrometer on a chip. With this technology a complete GC/MS could be reduced to the size of a shoebox, resulting in a revolution in the fieldability and cost of GC/MS based CEMS. Westinghouse plans to be an original equipment supplier to instrument manufacturers who would produce integrated CEMS.

Advantages:

- Excellent sensitivity: sub-ppb.
- Continuous
- Good selectivity

Disadvantages:

- May not have sufficient specificity in HWI stack environment, in which case must couple with GC.
- Expensive, although miniaturization may drastically reduce costs in the future

2.5.4 Ion Mobility Spectroscopy

IMS systems, described in Section 2.4.4, are available for some specific organic compounds and for classes of compounds. Typical detection limits are on the order of 1 ppb with response times on the order of 30 seconds (Environmental Technologies Group Inc., 1994). ETG, a maker of IMS CEMS, estimates that they could develop an analyzer for chlorinated organics in 6 months for $50,000. The cost of such a device would also be in the $50,000 range.

Advantages:

- Excellent sensitivity: down to 1 ppb
- Continuous, good time response
- Relatively inexpensive.

Disadvantages:

- Low specificity, but may be good for classes of compounds.

2.5.5 DOAS

The Opsis systems described previously can simultaneously detect some acid gases, NO_x, SO_x, water, and many organics. Opsis is designed for open path measurements and for cross stack monitoring. Detection limits depend on the measurement path length: for a 20 foot path, the detection limit for most species is in the ppm range (ABB Power Plant Controls, 1994). Opsis is TUV approved in Germany.

Advantages:

- Specific compounds can be detected
- Multicomponent measurements.
- In-situ.

Disadvantages:

- Relatively expensive.
- Detection limits not low enough without concentration (but system is designed for in-situ measurements)
- The list of organics that can be detected is restrictive.

2.5.6 FTIR

FTIR systems, described in Section 2.4.6, are available from a variety of vendors and work has been underway for several years using FTIR spectrometers for the measurement of organic compounds in ambient air (long path monitoring for fence lines, eg.). The EPA has also been funding the development and validation of FTIR methodology for stack sampling and monitoring (Entropy Environmentalists, Inc., 1993). The FTIR technique is attractive because it is capable of detecting a wide range of compounds (reference spectra for 105 HAPs are currently available) at the 0.5 - 5 ppm level. It can detect multiple compounds simultaneously (up to 10 to 20), and the measurement time is on the order of minutes. Sample concentration is necessary to make measurements at the sub-ppm levels of most PIC's in stacks. The results of recent EPA validation tests using several different sampling techniques were the following: direct sampling of hot, humid stack gas resulted in the quantitative measurement of 23 compounds at the 10 ppm level (21 compounds gave non-valid results), use of a condenser to knock out water vapor gave quantitative results for 24 compounds at the 10 ppm level (22 compounds gave non-valid results), and use of an adsorption/desorption system gave quantitative results for 11 compounds at the 0.5 ppm level (13 compounds gave non-valid results). Factors affecting the results are sample loss in the sample transport system, spectral interferences (water vapor), and efficiency of the sorbent for various compounds. However, no commercial system is currently available that can measure PIC concentrations at the 1 to 100 ppbv level at which most species occur.

Advantages:

- Multicomponent, species specific analysis

Disadvantages:

- Moderately expensive
- Detection limits not low enough without concentration

2.5.7 UV Photo-ionization

A monitor for particle bound PAH using photoelectric detection is commercially available

from EcoChem. The measurement is performed on a stack slip-stream that is heavily diluted with ambient air. A UV lamp is used to photo-ionize PAH molecules on the surface of particles. The free electrons are then accelerated by an electric field to an electrode and the resulting current is measured (EcoChem, 1994 and Niessner and Wilbring, 1989). This instrument has been evaluated by the EPA for ambient monitoring (Wilson, et al., 1993), and is currently being evaluated by the Combustion Research Branch of the EPA Office of Research and Development for use as a stack emissions monitor.

In the ambient air evaluation cited above, it is noted that instrument response varies from species to species: the photoelectric threshold is lower for larger PAH. The response is also larger for PAH on smaller particles. Thus quantitative measurements are made by correlating the monitor signal with PAH concentration measured by independent means. It has been found that this calibration is independent of the type of aerosol within a factor of two. Detection limits are on the order of 10 ng/m^3. Instrument response is also likely to be affected by water concentration, which quenches the photoelectric emission. For these reasons, it was concluded that the monitor produces semi-quantitative results and that its use is most appropriate as a screening instrument.

Evaluation of the instrument for stack monitoring by the Combustion Research Branch has also shown a good correlation of instrument response with conventional PAH measurements. Additional field testing by EPA has shown that the instrument can not be used downstream of an ESP (the charged particles generated by the ESP interfere with the measurement). Since about half of all facilities use ESP's, use of this instrument for compliance monitoring does not appear to be feasible.

Advantages:

- Excellent sensitivity to particle borne PAH as a class
- Good time response
- Inexpensive

Disadvantages:

- Only particle bound PAH
- Not quantitative
- Can not be used downstream of an ESP

2.5.8 LIF

Laser Induced Fluorescence has been proposed as a potential monitoring method for PAH and dioxins/furans. The EPA Office of Research and Development has carried out a feasibility

study of this approach (Radian Corp., 1993). A previous study (Radian Corp., 1991) had concluded that LIF was the most promising approach to take. As part of the feasibility study, pure vapor spectra of 2,3,7,8-tetrachloro dibenzo-p-dioxin, 1,2,3,7,8-pentachloro dibenzo-p-dioxin, 2,3,7,8-tetrachloro dibenzofuran, octachloro dibenzofuran, and benzo-(a)-pyrene were obtained with detection limits ranging from 0.01 to 24.6 ng/m^3. The spectrum for each of these compounds was unique, with peak positions ranging from 335 to 453 nm. On the basis of this study it was recommended that a LIF system based on excitation at 308 nm using a XeCl laser be developed.

There are, however, many potential problems with this approach. The spectra from large aromatic and chlorinated aromatic hydrocarbons are broad. Thus in actual stack conditions, where many different PAH and chlorinated PAH species are present simultaneously, the resultant spectrum is a superposition of the many individual spectra from which it is unlikely that species specific information can be derived. LIF is also subject to effects that may make quantitative measurement difficult: quenching of the fluorescence, self-absorption, and light scattering by particles. It is doubtful that detection limits in the field would even closely approach those derived from pure component studies in the lab.

The association of broadband fluorescence with PAHs has been known for some time (Miller et al., 1982) in the combustion research community. Prof. Sarofim's group at MIT has correlated PAH fluorescence excited by an argon ion laser at 488 nm with total PAH concentration determined by traditional means, and has a patent pending on their approach (Thijssen et al., 1994). They estimate the detection limit for total PAH to be in the parts per billion range. Because of the difficulties mentioned in the preceding paragraph, and the fact that the fluorescence yield varies from species to species (some do not fluoresce at all), it is not clear that this approach can be used to determine absolute PAH concentrations with confidence. Thus, while LIF appears to be a promising monitor for trends in PAH emission, more research is needed to determine if it can used for compliance purposes. Technolas, a German company, is currently field testing a prototype. Their first series of tests, at an MWC, were not successful due to the fact that actual PAH concentrations were below the detection limit of the instrument. They are currently redesigning the instrument to lower the detection limit, and plan to conduct more field test soon.

Advantages:

- Excellent sensitivity to vapor phase PAH as a class
- Good time response

Disadvantages:

- Only vapor phase PAH
- Not quantitative

2.5.9 Summary and Conclusions

The various organic compound CEMS and their capabilities and other characteristics are summarized in Table 2-19. Direct sample mass spectrometry offers the best combination of continuous operation, adequate detection limits, and multiple species resolution/capability. Commercially available systems are already available, and there will soon be many entrants/variants on the market. In stack detection of PIC's has been demonstrated, although further work is needed to demonstrate that the results are quantitative. Optically based instruments, such as DOAS (Opsis) and FTIR systems, offer continuous operation and multi-species capabilities, but do not have sufficient sensitivity to measure chlorobenzene at sub 100 ppbv levels.

It should be noted that, with the exception of the PM bound PAH meter, all of the approaches discussed in this survey are for the measurement of *volatile* organics only. Most semi-volatile and all condensed organics are beyond the capabilities of the CEMS measurement technologies currently under development. Given this limitation, however, it is likely that CEMS capable of measuring volatile and some semi-volatile PIC's could be available in under two years. Since PCDD/F concentrations are so small as to be below any likely detection limits available in the next few years, identification of surrogates from the mixture of PIC's that are detectable is of prime importance.

2.6 SUMMARY AND CONCLUSIONS

2.6.1 PM CEMS

Several different types of device are currently commercially available for continuous monitoring of PM emissions, and many are installed worldwide. Light scattering based devices are TUV approved and used for compliance monitoring in Germany. Use of these devices for compliance monitoring depends on calibration against manual gravimetric methods since they measure a secondary property of the particulate rather than mass. The feasibility of using PM CEMS for compliance therefore hinges on the stability of the calibration as the properties of the particulate change with process conditions. The German experience is that, for well controlled sources, the calibration relation is sufficiently stable. Although demonstration that this is the case at hazardous waste burning facilities in the US has not yet been carried out, all of the available information indicates that the use of these CEMS for compliance monitoring should be feasible.

2.6.2 Mercury CEMS

Several different approaches to monitoring total mercury are under development, and one device is commercially available. This device has TUV laboratory approval, and is currently undergoing the field trial phase of the certification process. All of the devices have demonstrated

at least the ability to measure elemental mercury and mercury chloride. Since these are the major mercury species emitted, monitoring for "total" mercury appears feasible. In fact, in principle these monitors should actually detect all speciated mercury. The one device that is currently available also measures PM bound mercury. Since this is accomplished by thermal desorption, with modification all of the device under development should also be able to measure PM bound mercury. A CEMS for total mercury thus appears feasible, although this needs to be demonstrated through field comparisons with the EPA reference method.

2.6.3 Acid Gas CEMS

Many different types of device for monitoring HCl are currently available and installed worldwide. Several are TUV approved and used for compliance monitoring in Germany. Several have also been tested by the EPA in an HCl CEMS demonstration program and been found to perform satisfactorily. The feasibility of using a CEMS for compliance monitoring of HCl can thus be considered to be established. This is not the case for monitoring of Cl_2. A couple of different monitoring approaches are available: UV DOAS (Opsis) and mass spectrometry. Of these, only Opsis is TUV approved, although not for Cl_2, and only Opsis is widely installed. Monitoring for Cl_2 thus appears to be feasible, but this needs to demonstrated in the field against EPA reference methods.

2.6.4 Multi-metals CEMS

No CEMS for monitoring multi-metals are currently available. Several different technologies are currently under development, and two to three prototype systems are entering the field test phase. Although these devices are promising, by the time any of them reach and pass the demonstration phase against EPA reference methods at least another year will have passed, and it is probably a minimum of two years before any system would be commercially available.

2.6.5 Organics CEMS

A variety of approaches for simultaneously monitoring multiple organic species are under development. Of these, direct sample mass spectrometry is the most promising in due to its low (sub ppb) detection limits. There are many vendors working on this approach, and at least one system is already commercially available. This system has undergone some limited field testing in both Europe and Canada, and is currently installed on three incinerators in Europe. In stack measurement of PIC's at the 1 to 100 ppb level has been demonstrated. However, quantitative measurement still needs to be demonstrated by comparison with EPA reference methods in a field trial in this country. In addition, there is a need for detailed PIC emission data from hazardous waste burning facilities in order to determine which species to regulate and at what levels. If demonstration of a CEMS for PIC's is successful, then there is strong potential for surrogate (eg.,

chlorobenzene) monitoring for PCDD/F.

TABLE 2-1. SUMMARY OF PM CEMS

Type	Principle	Maker	Available/Cost	Address/Phone/Contact
O	Opacity	Monitor Labs, Inc. & Others	Yes	74 Inverness Dr. East Englewood, Co 80112 (303) 792-3300 Sarah Hamilton
O	Time Dependent Transmission	BHA	Yes $15K	8800 East 63rd St. Kansas City, MO 64133 (816) 356-8400 Mark Santschi
O	Forward Scatter	Insitec	Yes $28K	2110 Omega Rd., Suite D San Ramon, CA 94583 (510) 837-1330 Michael Bonin
O	Back Scatter	Environmental Systems Corp.	Yes $10K	200 Tech Center Dr. Knoxville, TN 37912 (615) 688-7900 Robert Nuspliger
O	90° Scattering	Sick Optic-Electronic Inc. (Germany)	Yes $18K	7694 Golden Triangle Dr. Box 444-240 Eden Prairie, MN 55344 (612) 941-6780 Stephen Wisker
E	Beta Gauge	Emission S.A. (France)	Yes $35K	Environment U.S.A. 302 Capistrano Ave. Shell Beach, CA 93449 (805) 773-4255 Tony Griguoli
E	Oscillating Element	Ruprecht & Pataschnick Co., Inc.	Yes	25 Corporate Circle Albany, NY 12203 (518) 452-0065
P	Triboelectric	Auburn International, Inc.	Yes $10K	8 Electronics Ave. P.O. Box 2008 Danvers, MA 01923 (508) 777-2460 Chris Reiner
P	Acoustic Energy	Jonas, Inc.	Yes $12K	1113 Faun Rd. Wilmington, DE 19803 (302) 478-1375 Ravi Mathur

TABLE 2-2. SUMMARY OF PM CEMS PERFORMANCE SPECIFICATIONS

Principle	**Maker**	**Load Range**	**Size Range**	**Issues**
Time-dependent Transmis-sion	BHA	0.000004 - 4 gr/dscf	0.3 - 75 µm	1) Response depends on particle composition and size distribution. 2) Must assume particle density (calibrate) to obtain mass measurement.
Forward Scatter	Insitec	0.006 - > 1 gr/dscf	1 - 100 µm	1) Response depends to some extent on particle composition and size distribution (less so than for back scattering and opacity). 2) Must assume particle density (calibrate) to obtain mass measurement.
Back Scatter	Env. Systems Corp.	0.0005 - 8 gr/dscf	0.05 - 10 µm	1) Response depends on particle composition and size distribution. 2) Must assume particle density (calibrate) to obtain mass measurement.
Side Scatter	Sick Optic	$2X10^{-6}$ - 0.01 gr/dscf	0.1 - 50 µm	1) Response depends on particle composition and size distribution. 2) Must assume particle density (calibrate) to obtain mass measurement.
Tribo-electric	Auburn	> $5X10^{-5}$ gr/dscf	> 0.5 µm	1) A mass response will depend on resistivity and density of the particles. 2) Small particles will follow the flow and not impact the probe. 3) Effect in (2) and limited sensitivity to smaller particles means response will be dependent on size distribution and velocity.
Acoustic Energy	Jonas, Inc.	0 - 0.05 gr/dscf estimated for typical stack conditions (depends on flow velocity, size distribution, and density).	> 10 um	1) Response depends on particle velocity. 2) Small particles will follow the flow and not impact the probe. 3) Effect in (2) and limited sensitivity to smaller particles means response will be dependent on size distribution.
Beta Gauge	Emissions S.A.	1.25 mg/m^3 based on a sampling time of two minutes	All	1) Losses in extractive sampling.

TABLE 2-3. PARAMETERS AFFECTING PM CEMS

Type/Principle	**Parameter/Issue**
Optical	1. Particle size distribution 2. Composition (through effect on index of refraction). 3. Density
Probe/Tribo-electric	1. Particle size distribution 2. Flow velocity 3. Resistivity 4. Density
Probe/Acoustic Energy	1. Particle size distribution 2. Flow velocity
Extractive/Beta Gauge	1. Sampling Losses

TABLE 2-4. SUMMARY OF PM CEMS REGULATIONS

	German Regulation (for PM CEMS)	**EPA Regulation**
Sensitivity to temperature in the range of -20 to 50 C	< 2% of full scale	None
Sensitivity to supply voltage fluctuations of -15 to +10 %	< 2% of full scale	None
Response to a set of internal calibration standards	+/- 2% of value of standard	None
Zero point drift	< 2% over the maintenance interval	<2.5% during 7 day check of performance. specs, during normal operation <5% per day (requires recalibration). Drift is excessive if >5% for 5 consecutive days or >10% at any check, and maintenance is required. Check required at least once per day.
Sensitivity drift	< 2% over the maintenance interval	Same as above
Automatic sensitivity correction	< 6% over the maintenance interval	Same as above
Data Availability	> 90 %	None
Instrument response check (see section 2.2.1 item 3)	Yearly	Quarterly cylinder gas audits
Calibration check (against manual reference method)	Every 3 to 5 years	Yearly RATA's

TABLE 2-5. SUMMARY OF MERCURY CEMS

Maker	**Available/Cost**	**Address/Phone/Contact**
PSI	Under development	Physical Sciences, Inc. 20 New England Business Center, Andover, MA 01810 (508) 689-0003 Larry Piper
ADA	Under development	ADA Technologies, Inc. 304 Inverness Way South Suite 110 Englewood, CO 80112 (303) 792-5615 Richard Schlager
Verewa	Yes, $130K	Euramark 834 E. Rand Rd., Suite 6 P.O. Box 823 Mount Prospect, IL 60056 Hans Brouwers
Senova	Under development, estimated cost $50K	Senova Corp. 1435 N. Hayden Rd. Scottsdale, AZ 85257 (602) 970-6355 Ian Sorensen
ABB (Elemental only)	Yes, $120K	ABB Power Plant Controls 2 Waterside Crossing Windsor, CT 06095 (203) 285-6893 Gary Teodosio

TABLE 2-6. SUMMARY OF ACID GAS CEMS

I. NDIR Based

Maker	**Available/Cost**	**Address/Phone/Contact**
Bodenseewerk	Yes (S) $150 - 200K (HCl and NOx, SOx, CO, CO2, H20, CH4, NH3)	Altech Systems Corp. 11969 Challenger Ct. Moorpark, CA 93021 (805) 529-9955 Rich Brown
Servomex Co., Inc.	Yes (S) $30K (HCl)	90 Kerry Place Norwood, MA 02062 (800) 862-0200 Lynne Baron
Air Instruments and Measurements, Inc. (AIM)	Yes (S) $40 K (in-situ) $55 K (hot/wet extractive) (HCl, multi-component CEMS also available)	13111 Brooks Dr., Suite D Baldwin Park, CA 91706 (818) 813-1460 Harold Lord
Thermo Environmental Instruments Inc. (TECO)	Yes (S) $12K (HCl)	Eight West Forge Parkway Franklin, MA 02038 (508) 520-0430 John Mclean

II. Ion Selective Electrode Based

Maker	Available/Cost	Address/Phone/Contact
TessComm	Yes (S) $25K (HCl)	P.O. Box 600 Clairton, PA 15025 (412) 233-5782 Lou Colonna
Bran & Luebbe	Yes (S) $60K (HCl. Units also available for HF)	Analyzing Technologies, Inc. 103 Fairview Park Dr. Elmsford, NY 10523 (708) 520-0700 Tom Iervolino
Compur	No information available	
Kyoto	No longer marketed in the US	
Severn Science Instruments	Yes (S) $40K (HCl)	Mission Instruments 26705 Loma Verde Mission Viejo, CA 92691 (714) 582-0889 George Sotter

III. Ion Mobility Spectroscopy Based

Maker	Available/Cost	Address/Phone/Contact
Environmental Technologies Group, Inc. (ETG)	Yes (S) $15K ($Cl_2$ & HCl, F_2 & HF, Br_2 & HBr, I_2)	1400 Taylor Ave. P.O. Box 9840 Baltimore, MD 21284 (410) 339-3146 Alan Bickel

IV. UV Spectroscopy Based

Maker	Available/Cost	Address/Phone/Contact
ABB Power Plant Controls	Yes (S) (Cl_2, HCl, HF, and many others) $125K	2 Waterside Crossing Windsor, CT 060095 (203) 285-6796 Mike Hartman
Ametek	Yes, but not for stack sampling. (HCl)	455 Corporate Blvd. Newark, DE 19702 (800) 222-6789 Brian Reed

V. Colormetric Based

Maker	Available/Cost	Address/Phone/Contact
MDA	Yes, but not for high H2O applications. No hot/wet sampling system. Thus not appropriate for HWI stacks.	405 Barclay Blvd. Lincolnshire, IL 60069 (800) 344-4632

VI. FTIR Based

Maker	Available/Cost	Address/Phone/Contact
KVB	Yes (S) < $100K	9342 Jeronimo Irvine, CA 92718 (714) 587-2300 William Cottrell (703-694-5778)
Enviroplan	Yes (S)	3 Becker Farm Rd. Roseland, NJ 07068 (201) 994-2300
Rosemount	Yes (S)	1201 North Main St. P.O. Box 901 Orrville, OH 44667 (800) 628-1200

VI. MS Based

Maker	Available/Cost	Address/Phone/Contact
Extrel	Yes (A) $120K w/o sampling system. (HCl, Cl_2, HF, F_2, I2, Br_2, HBr)	575 Epsilon Dr. Pittsburgh, PA 15238 (713) 661-6569 Joe Schwab
Fisons	Yes (A)	32 Commerce Center Cherry Hill Dr. Danvers, MA 01923 (508) 777-8034 Jason Cape

TABLE 2-7. SUMMARY OF ACID GAS CEMS

Type	**Detection Limit**	**Species**	**Comments**
NDIR	Approx. 1 ppm	HCl	- Inexpensive - Multicomponent for major species
ISE	Sub-ppm	HCl	- Inexpensive
IMS	Sub-ppm	Total HCl + Cl_2	- Inexpensive - Systems for HF and F_2, HBr and Br_2, I_2, Cl_2O also
UV	Approx. 1 ppm	HCl, Cl_2, HF	- In-situ - Multicomponent - Expensive
FTIR	Approx. 1 ppm	HCl, HF, HBr	- Multicomponent - Moderately expensive
MS	Sub-ppm	All acid gases	- Multicomponent - Expensive

TABLE 2-8. LIST OF METALS CEMS DEVELOPERS

Developer	Method	Contact	Address	Phone Number
3M	3M	Dana Schnobrich	3M Co. St. Paul, MN 55133	612-458-2500
Chester Environmental	HEST	John Cooper	12242 S.W. Garden Place, Tigard, Oregon 97223	503-624-2773
Midwest Research Inst.	SPICAP	Gary Hinshaw	425 Volker Blvd. Kansas City, MO, 64110	816-753-7600
NAWC China Lake	On-line ICP	Mike Seltzer	NAWC-Weapons Div. China Lake, CA 93555	619-939-1608
DOE Morgantown	On-line ICP	Bill Chisholm		304-291-4730
ADA Technologies	On-line ICP	Mike Durham	304 Inverness Way South Englewood, CO 80112	303-792-5615
Sandia - Livermore	LASS	Nina Bergen-French	Sandia National Laboratories, Livermore, CA	510-294-2046

TABLE 2-9. HEST DETECTION LIMITS ($\mu g/m^3$)

Element	**HEST[a]**	**HEST[b]**	**HEST[c]**	**HEST[d]**
Sb			0.096	0.360
As	0.01	0.012	0.029	0.120
Cd	0.052	0.080	0.096	0.360
Cr	0.020	0.020	0.029	0.120
Pb			0.058	0.240
Hg	0.006	0.006	0.048	0.144
Ni	0.008	0.016	0.029	0.120
Se	0.005	0.006	0.029	0.120

($2.5m^3$ sample at 20L/min takes 2 hours, $0.2m^3$ sample at 20L/min takes 10 minutes)
a - Particles, $2.5m^3$ sample, to date
b- Vapor, $2.5m^3$ sample, to date
c- Particles, $0.2m^3$ sample, potential
d- Vapor, $0.2m^3$ sample, potential

TABLE 2-10. X-RAY ATTENUATION FACTORS

Element	**Attenuation Factor**
Cr	0.92
Mn	0.93
Ni	0.96
Zn	0.95
Hg	0.98
As	0.98
Se	0.99
Pb	0.99
Cd	1.0
Sb	1.0

TABLE 2-11. ESTIMATED ON-LINE ICP DETECTION LIMITS

Element	**Solution Detection Limit (ug/L)**	**Airborne Detection Limit (ug/m^3)**
Sb	40	61
As	30	4
Be	0.1	0.01
Cd	2	0.2
Cr	3	0.3
Co	3	0.5
Pb	25	3
Mn	1	0.2
Hg	12	2
Ni	4	0.6
Se	30	5

TABLE 2-12. MORGANTOWN ICP DETECTION LIMITS

Element	**Detection Limit (µg/m^3)**[1]
As	390
Cd	12
Ca	0.095
Cr	1.1
Fe	5.1
Pb	140
Mg	0.23
Hg	430
Se	2400
Ti	1.6
V	1.4
Zn	190

[1] R.R. Romanowski, A.S. Viscomi, and W.P. Chisholm, Paper 662, Book of Abstracts-The Pittsburgh Conference, 1991

TABLE 2-13. LASS DETECTION LIMITS

Element	**Detection Limit (μg/m^3)**
As	15
Sb	35
Be	<0.1
Cd	2
Cr	1
Co	2
Pb	250
Mn	<0.25
Hg	15
Ni	40
Se	160

TABLE 2-14. CURRENT DETECTION LIMITS [µg/m^3]

Element	**Method 29[a]**	**Method 29[b]**	**HEST[c]**	**HEST[d]**	**SPICAP[e]**	**On-line ICP[f]**	**LASS**
Sb	3.8(0.35)	1.9(0.2)		0.360	1.6		35
As	6.4(0.15)	3.2(0.05)	0.01	0.012	2.6	390	15
Be	0.035 (0.025)	0.029 (0.015)			0.015		<0.1
Cd	0.5(0.01)	0.25 (0.005)	0.052	0.080	0.2	12	2
Cr	0.85(0.1)	0.4(0.05)	0.020	0.020	0.35	1.1	1
Pb	5.0(0.1)	2.5(0.05)			2.1	140	250
Mn	0.25(0.1)	0.1(0.05)			0.1		<0.25
Hg	0.3	1.5	0.006	0.006	0.01	430	15
Ni	1.8	0.9	0.008	0.016	0.75		40
Se	9.0(0.25)	4.5(0.15)	0.005	0.006	3.8	2400	160

(2.5m3 sample at 20L/min takes 2 hours, 0.2m3 sample at 20L/min takes 10 minutes)
a - Front half, 2.5m3 sample, ICP (GFAAS)
b - Back half, 2.5m3 sample, ICP (GFAAS)
c - Particles, 2.5m3 sample, to date
d - Vapor, 2.5m3 sample, to date
e - sample rate 200L/min, liquid flow rate 10 ml/min, 150 ml liquid volume, for a 15 minute time constant
f - DOE Morgantown

TABLE 2-15. POTENTIAL DETECTION LIMITS [$\mu g/m^3$]

Element	**Average Emissions**	**BIF Rule Limits**	**HEST[a]**	**HEST[b]**	**SPICAP[c]**	**On-line ICP[d]**	**LASS**
Sb			0.096	0.360	1.6	6	35
As	2.28	128	0.029	0.120	2.6	4	15
Be	0.57	230			0.015	0.01	<0.1
Cd	34.8	311	0.096	0.360	0.2	0.2	2
Cr	9.6	44	0.029	0.120	0.35	0.3	1
Pb	215	5000	0.058	0.240	2.1	3	250
Mn			0.029		0.1	0.2	<0.25
Hg	5.15	4400	0.048	0.144	0.01	2	15
Ni			0.029	0.120	0.75	0.6	40
Se			0.029	0.120	3.8	5	160

($2.5m^3$ sample at 20L/min takes 2 hours, $0.2m^3$ sample at 20L/min takes 10 minutes)

a - Particles, $0.2m^3$ sample, potential

b - Vapor, $0.2m^3$ sample, potential

c - sample rate 200L/min, liquid flow rate 10 ml/min, 150 ml liquid volume, for a 15 minute time constant

d - China Lake, estimated

TABLE 2-16. COMPARISON OF METALS CEMS

CEMS	Advantages	Disadvantages	Technical Issues	Operating Costs	Maintenance (Costs)
3M	Low development and installation costs	Long sampling times, manual, off-site analysis: "Semi-Continuous"	CIF performance	High: labor, filters, analysis	Low
HEST	archivable samples, good detection limits (<<M29), easy calibration	Extractive sampling, Be not detectable by XRF, batch sampling and analysis: response time on order of tens of minutes	Probe accumulation, CIF performance	Low: filters	Moderate: potential problems with sample handling
SPICAP	Continuous liquid sampling system, probe rinse and calibration easy, good detection limits (<M29)	Separate scrubber required for Hg, response time on the order of tens of minutes	Particle capture and transport, particle size effects	Moderate: scrubber solution, ICP feed gases	Moderate-High: liquid handling system, nebulizer, and ICP may require frequent maintenance requiring some skill
On-line ICP	Simple, continuous sampling; real-time analysis	Extractive sampling, ultimate detection limits not known and background dependent (estimated =M29)	Probe accumulation, particle size effects, background	Moderate: ICP feed gasses	Moderate: ICP maintenance? (some skill required)
LASS	In-situ	Ultimate detection limits not known and background dependent (estimated >M29), current detection limits >>M29	Particle size and background effects	Low: few consumables	Moderate: Laser maintenance?, Optics cleaning and alignment (skill required)

TABLE 2-17. STATUS OF METALS CEMS

CEMS	**Current stage of development**	**Development Time**	**Backing**	**Patent protection**	**Measurement time**
3M	essentially developed	essentially developed	3M	No	days
HEST	some component testing, established technology	< 2 years	Chester Environ-mental, needs sponsors, has potential sponsors	Yes	< hour
SPICAP	conceptual, established technology	< 2 years	MRI internal, needs sponsors	Yes	< hour
On-line ICP	proof of concept laboratory testing, some prototype development	maybe < 2 years	1. DOD internal,. 2. DOE internal. 3. ADA internal, DOE SBIR, sponsors for commercializa-tion. 4. Battelle internal, needs sponsors	1. No 2. No 3. Yes? 4. ?	minutes
LASS	proof of concept laboratory testing	probably > 2 years	Sandia, DOE	No?	minutes

TABLE 2-18. SUMMARY OF ORGANIC COMPOUND CEMS

I. Fast Cycle GC

Maker/Developer	Available/Cost	Address/Phone/Contact
EPA Combustion Research Branch	No Vapor phase organics	(919) 541-2854 Jim Kilgroe
Army Chemical Warfare Agent Disposal Program	No Vapor phase chemical warfare agent	(410) 671-3337 Jerry Queen Ballistic Research Lab Aberdeen Proving Grounds, MD
University of Utah Dept. of Mechanical Engineering	No Vapor phase organics	(801) 581-8431 Bill McClennen

II. Direct Sample MS

Maker/Developer	Available/Cost	Address/Phone/Contact
DOE/Los Alamos National Labs	No Vapor phase organics	(505) 665-5735 Philip Hemberger
DOE/Oak Ridge National Labs	No Vapor phase organics	(615) 574-4862 Mark Wise
Entropy Environmentalists	No information available	(919) 781-3550 Laura Kenner
Extrel	Process MS available, $120K w/o sampling system	575 Epsilon Dr. Pittsburgh, PA 15238 (713) 661-6569 Joe Schwab
Hewlett Packard	Process MS available	3495 Deer Creek Rd. Palo Alto, CA 94304 (800) 227-9770
Finnigan MAT	Process MS available	355 River Oaks Parkway San Jose, CA 95134

III. Ion Mobility Spectroscopy Based

Maker/Developer	Available/Cost	Address/Phone/Contact
Environmental Technologies Group, Inc. (ETG)	No 6 months & $50K to develop for classes of organics	1400 Taylor Ave. P.O. Box 9840 Baltimore, MD 21284 (410) 339-3146 Alan Bickel

IV. UV Spectroscopy Based

Maker/Developer	Available/Cost	Address/Phone/Contact
ABB Power Plant Controls	Yes (S) Vapor phase organics $125K	2 Waterside Crossing Windsor, CT 060095 (203) 285-6796 Mike Hartman

V. FTIR Based

Maker/Developer	Available/Cost	Address/Phone/Contact
KVB	Yes (S) Vapor phase organics < $100K	9342 Jeronimo Irvine, CA 92718 (714) 587-2300 William Cottrell (703-694-5778)
Enviroplan	Yes (S) Vapor phase organics	3 Becker Farm Rd. Roseland, NJ 07068 (201) 994-2300
Rosemount	Yes (S) Vapor phase organics	1201 North Main St. P.O. Box 901 Orrville, OH 44667 (800) 628-1200

VI. UV Photo-Ionization

Maker/Developer	Available/Cost	Address/Phone/Contact
EcoChem	Yes (S) Particle bound PAH $25K	22605 Valerio West Hills, CA 91307 (818) 347-4369 E. Chikhliwala

VII. LIF

Maker/Developer	Available/Cost	Address/Phone/Contact
Technolas	No Vapor phase PAH. Field testing technique developed at MIT.	Frankfurt, West Germany 011-49-89-858560 Thomas Weber

TABLE 2-19. SUMMARY OF ORGANIC COMPOUND CEMS

Type	**Detection Limit**	**Species**	**Comments**
GC	ppb range	classes of organics and speciation	- periodic sample injection - several development efforts
MS	sub-ppb	speciated organics	- expensive - several development efforts - process instruments available from many makers
IMS	ppb range	classes of organics	- inexpensive - estimated 6 months & $50K to develop
UV	ppm range	speciated organics	- limited number of species detectable - in-situ - expensive
FTIR	ppm range	speciated organics	- concentrating sampling systems for lower detection limits under development - many makers
UV Photo-ionization	ng/m^3 range for total PAH	Particle bound PAH	- inexpensive - commercially available - not compatible with ESP's
LIF	ppb range for total PAH	Vapor phase PAH	-prototype field testing

FIGURE CAPTIONS

Figure 2-1. Example of CEMS calibrations carried out at three different plant operating conditions.

At each condition the particulate properties (for example, size distribution and/or index of refraction) are different. The spread of the data points at each condition is due to variation in PM mass loading for constant properties at that condition. The three dashed lines represent least squares linear fits to the CEMS response vs. actual PM loading at each condition. The correlations at each condition between CEMS response and PM loadings are good and distinctly different.

Figure 2-2. Example of a single calibration based on data at three different plant operating conditions.

This figure shows a single linear least squares fit (dashed line) to all of the data from the three conditions shown in Figure 2-1. The solid lines represent the 95% confidence interval of the fit. Note that the effect of performing a single fit to all of the data, which contains variation in the PM properties, compared to the three fits at each condition shown in Figure 2-1: the scatter of the data around the single fit is larger. However, this figure illustrates how the practice of performing a CEMS calibration over a range of plant operating conditions that may have varying PM properties works. The varying PM properties cause the scatter in the data, which is quantified by the 95% confidence bounds placed on the calibration. Specification of how good the correlation and how small the uncertainty must be can be achieved by setting a minimum value of the correlation coefficient and a maximum uncertainty at the emission limit for acceptance of the calibration.

Figure 2-3. Calibration of Sick RM200.

This figure shows the data from the first calibration of the Sick RM200 at a secondary lead smelter described in the TUV certification report. The dashed line is the linear least squares fit to the data which establishes the calibration relation between the RM200 output and the PM loading as determined by the manual reference method. The curved solid lines closest to the dashed line are the 95% confidence bounds on the calibration relation. Thus, if the RM200 output is 10 mA, using the calibration relation gives a PM loading of about 2.95 mg/m3 with a 95% confidence that the true PM loading is between 2.7 and 3.2 mg/m3. The solid lines furthest from the dashed line represent the tolerance interval bounding 75% of the population of all comparisons between the RM200 and the reference method at the 95% confidence level. That is, based on the data set shown, one can expect that for further testing that 75% of the data will fall inside the tolerance interval. Thus, the tolerance interval provides a criterion for judging, based on future comparisons of the RM200 with reference method data, whether the new data is consistent with the calibration relation. Both sets of solid lines, the confidence interval for the calibration relation and the tolerance interval, only extend as far as there is test data reflecting the fact that these statistical statements are valid only in the PM range covered by the calibration. In fact, the calibration

relation itself is only considered valid in this range also.

Figure 2-4. Calibration check for Sick RM200.

This shows the same calibration relation and statistical bounds from Figure 2-3 for the first calibration of the RM200 with data overlaid from the second and third calibrations. One can see that, although the data seems to be biased low with respect to the calibration relation, better than 75% of the data (11 out of 14 the points that are within the range of calibration 1) is bounded by the tolerance interval, and is thus consistent with the first calibration. Note that some of the data from calibrations two and three spans a wider range that was covered by the first calibration. This data cannot be rigorously compared to the first calibration, however, it also appears to be consistent with calibration 1 when the solid lines representing the tolerance interval are extrapolated.

Figure 2-5. Calibration of the Sick RM200 based on all of the data.

This figure shows the data from all of the calibrations performed during the suitability testing of the RM200. The master calibration relation based on all of this data, 95% confidence interval, and tolerance limits, as explained in the discussion of figure 3, are shown also (the solid lines for the confidence and tolerance intervals are not extended quite to the upper limit of the calibration range due to a fault in the graphics software). Note that with this many data points that the confidence interval for the calibration relation is very small, about +/- 4% at the middle of the calibration range.

Figure 2-6. Comparison of initial calibration to all of the data.

This figures shows a comparison between all of the calibration data and the calibration relation and confidence and tolerance intervals for calibration one (solid lines). The dashed line is the master calibration relation from Figure 2-5. The first calibration relation and confidence and tolerance intervals are consistent with all of the data and the master calibration within the range of the first calibration.

Figure 2-7. Reproducibility of the reference method measurements.

This figure shows the reproducibility of the duplicate reference method measurements taken during calibration three. The dashed line is a least squares fit to the data. Deviation of the data from this line represents the uncertainty associated with the measurements.

Figure 2-8. Reproducibility of the Sick RM200 measurements.

This figure shows the reproducibility of the RM200 measurements taken using units 4 and 5 during calibration three. The dashed line is a least squares fit to the data. Note that the uncertainty of the RM200 measurements is considerably less than that of the manual measurements shown in Figure 2-7.

Figure 2-9. Multi-metals CEMS detection limits.

Stack detection limits for the HEST, SPICAP, LASS, and on-line ICP multi-metals CEMS under development and for Method 29 are shown as a function of sampling time. Note that on-line ICP and LASS have no sample collection, and thus the detection limits are independent of time.

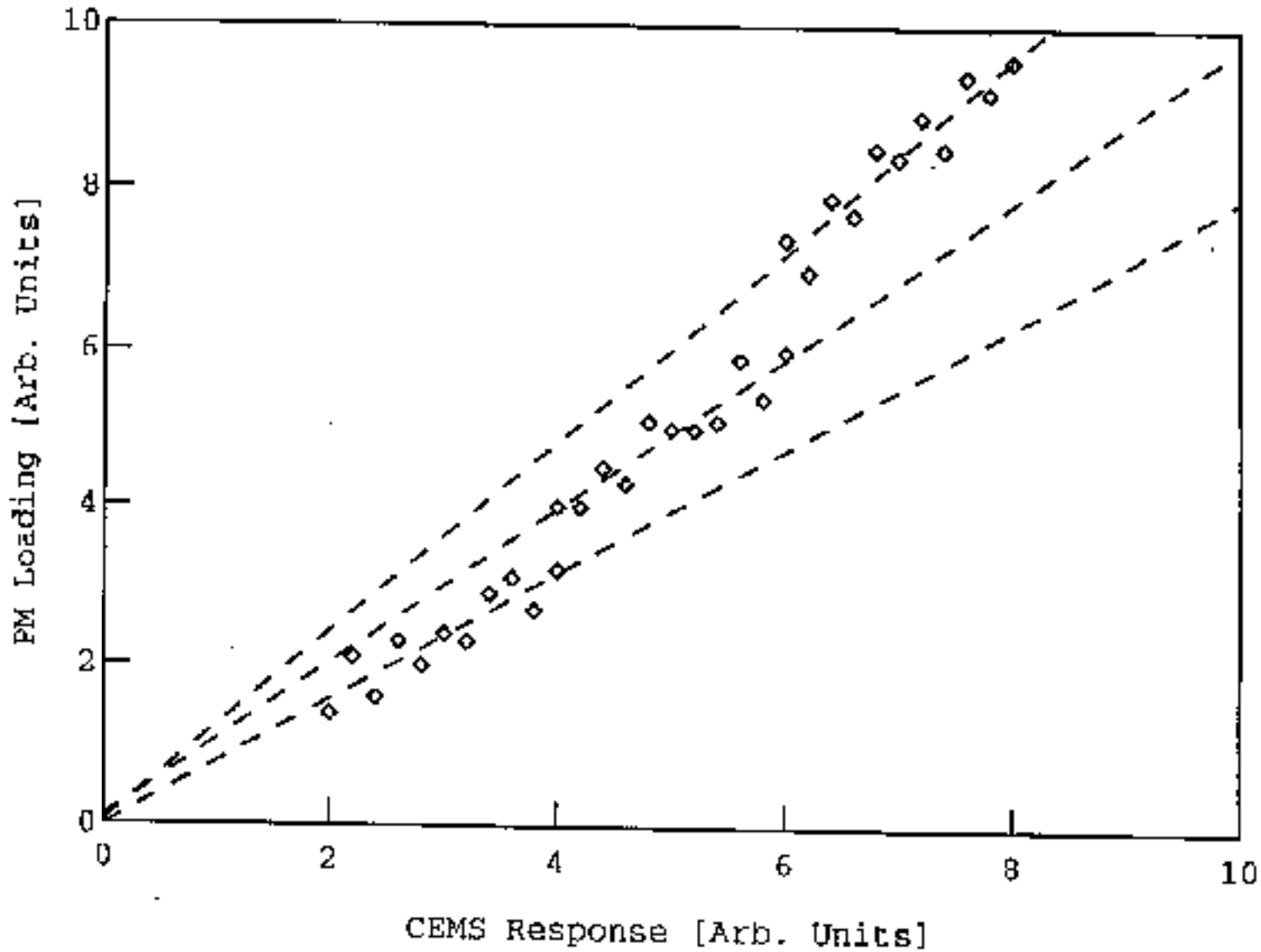

Figure 2-1. Example of CEMs calibrations carried out at three different plant operating conditions.

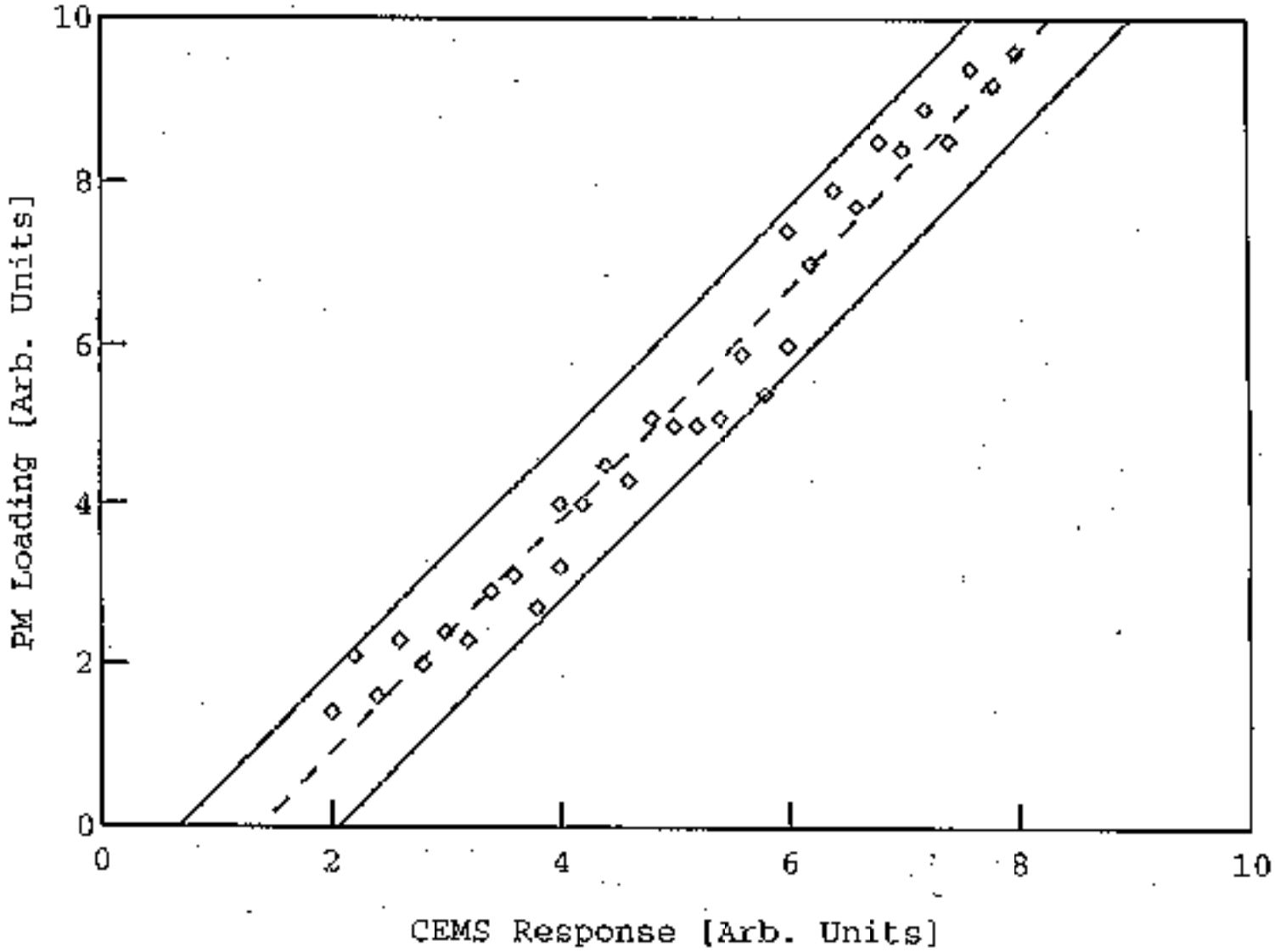

Figure 2-2. Example of a single calibration based on data at three different plant operating conditions.

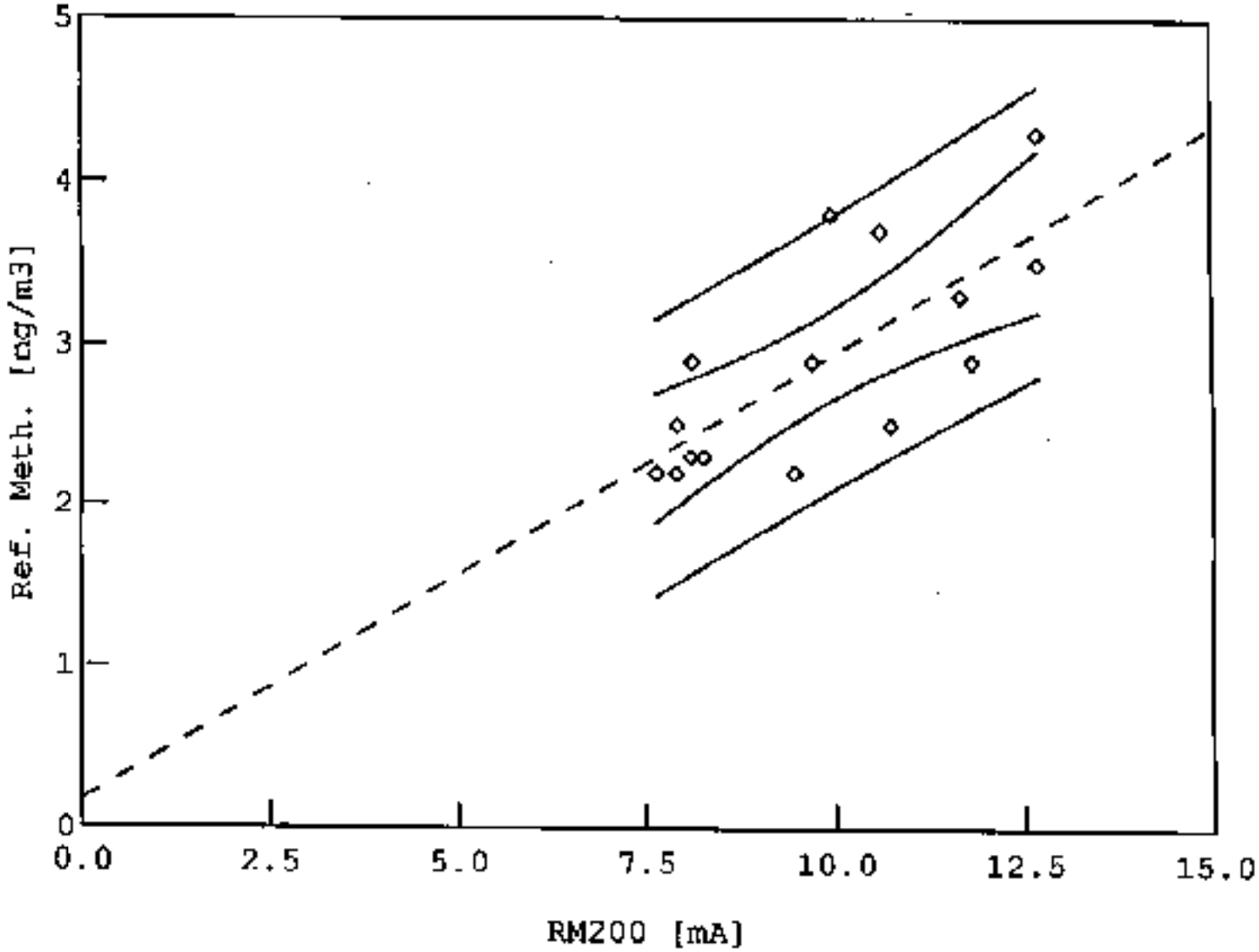

Figure 2-3. Calibration of Sick RM200.

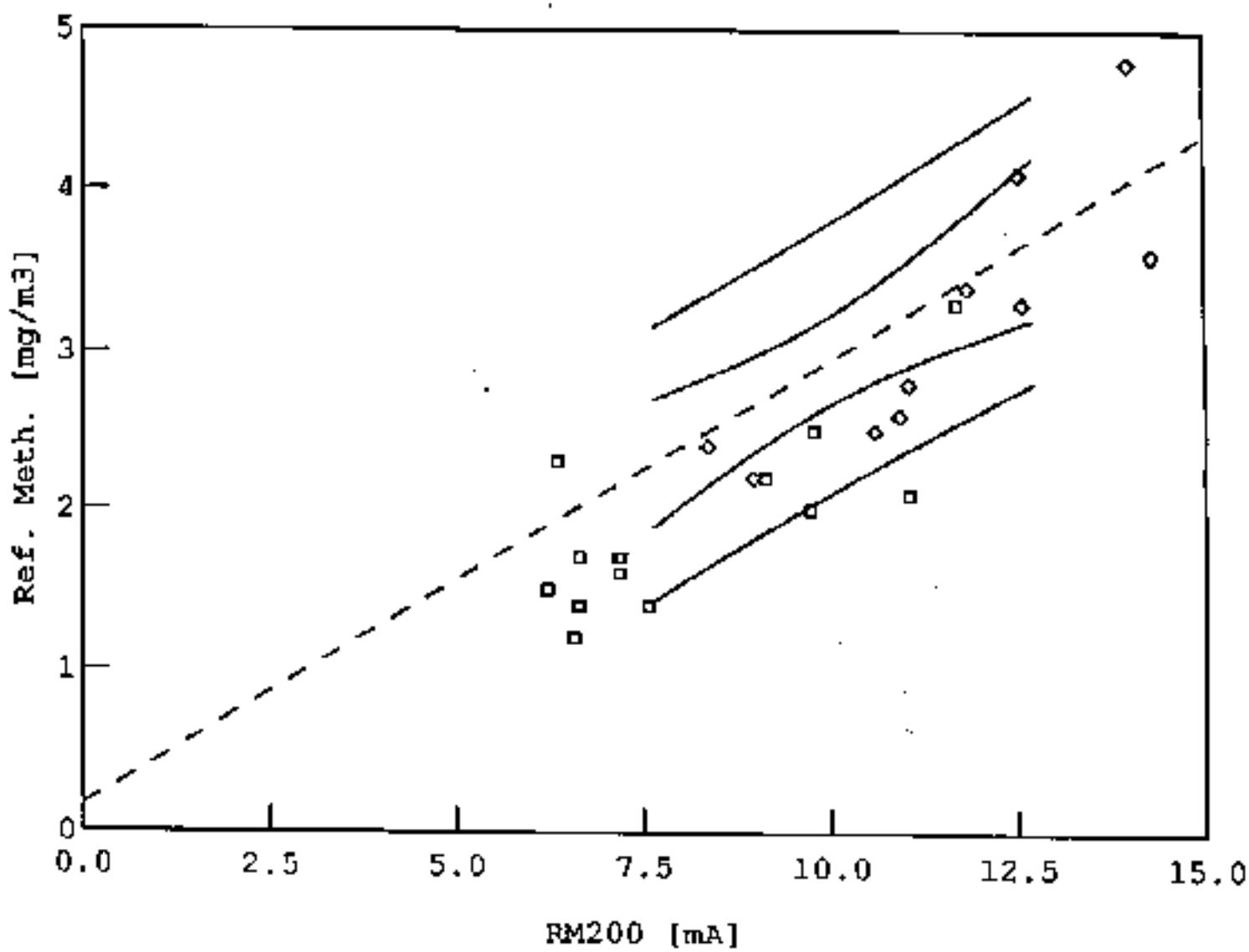

Figure 2-4. Calibration check for Sick RM200.

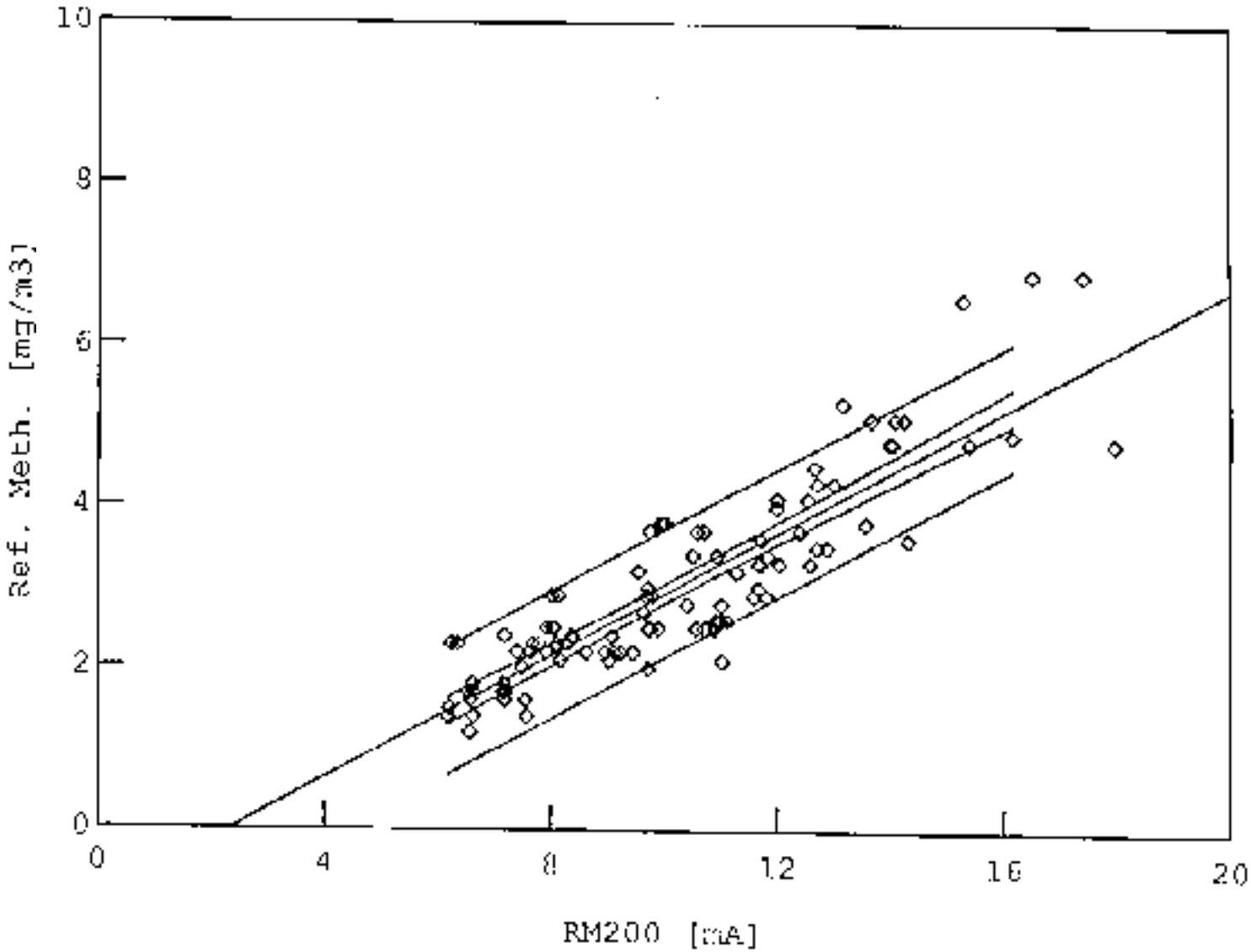

Figure 2-5. Calibration of the Sick RM200 based on all of the data.

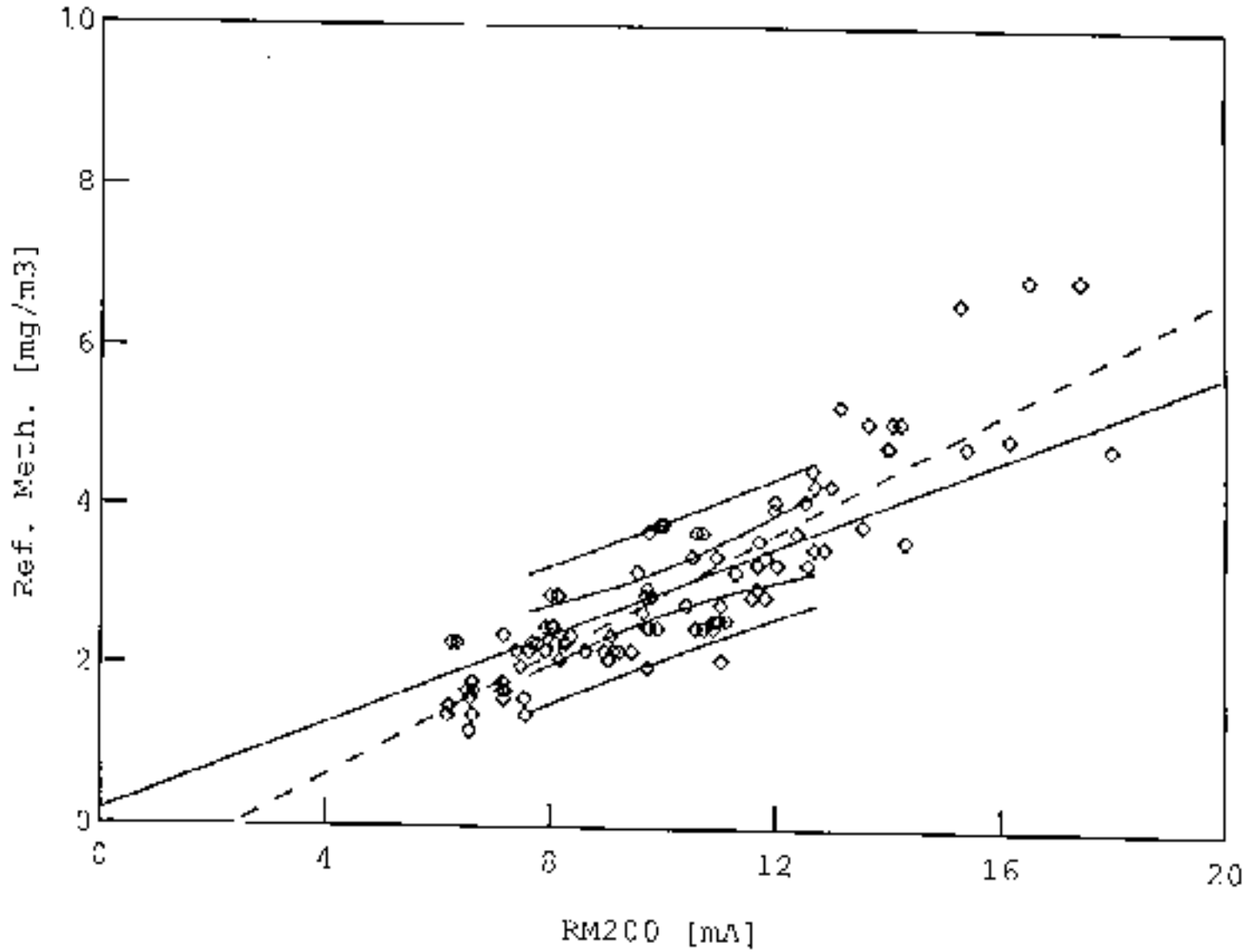

Figure 2-6. Comparison of initial calibration to all of the data.

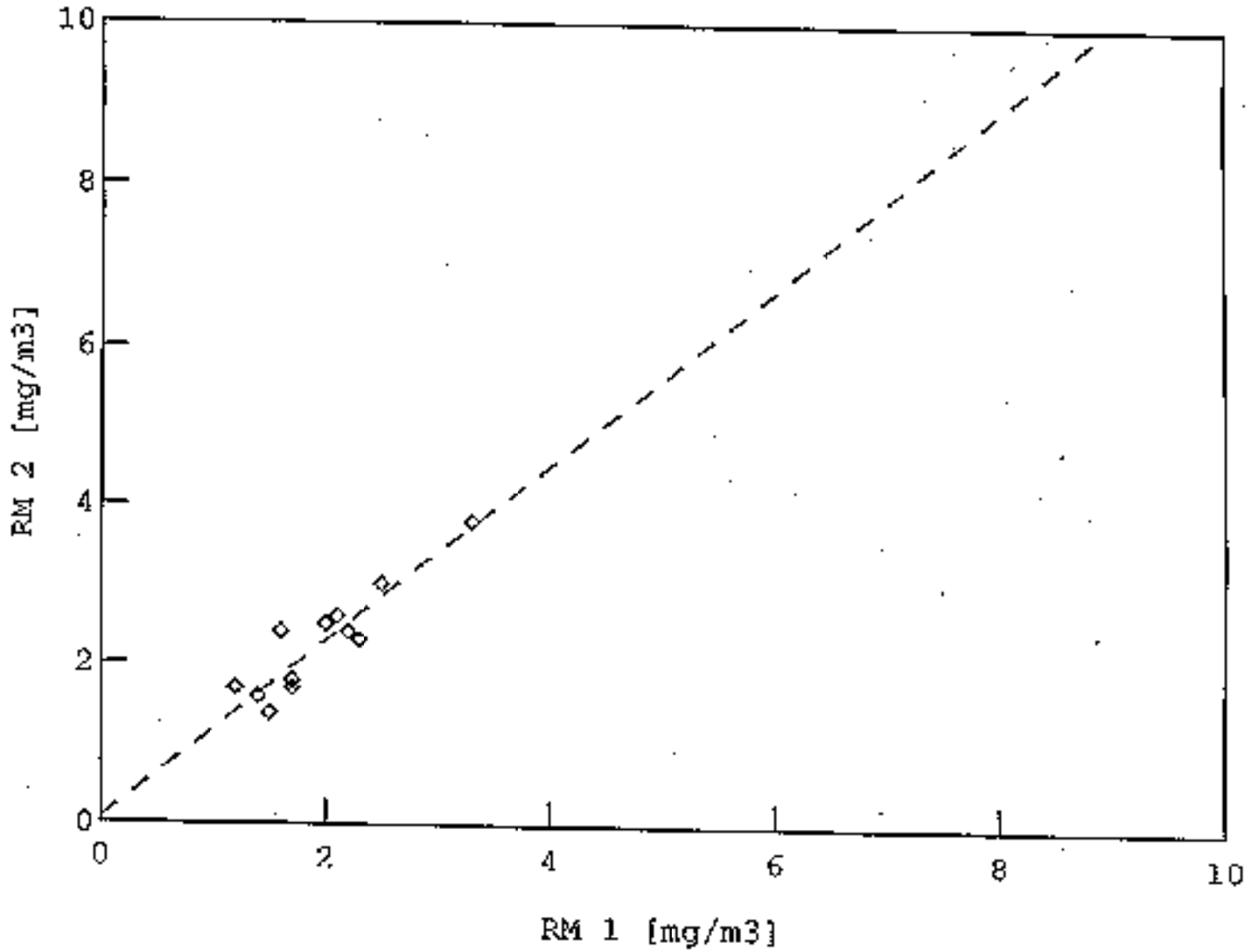

Figure 2-7. Reproducibility of the reference method measurements.

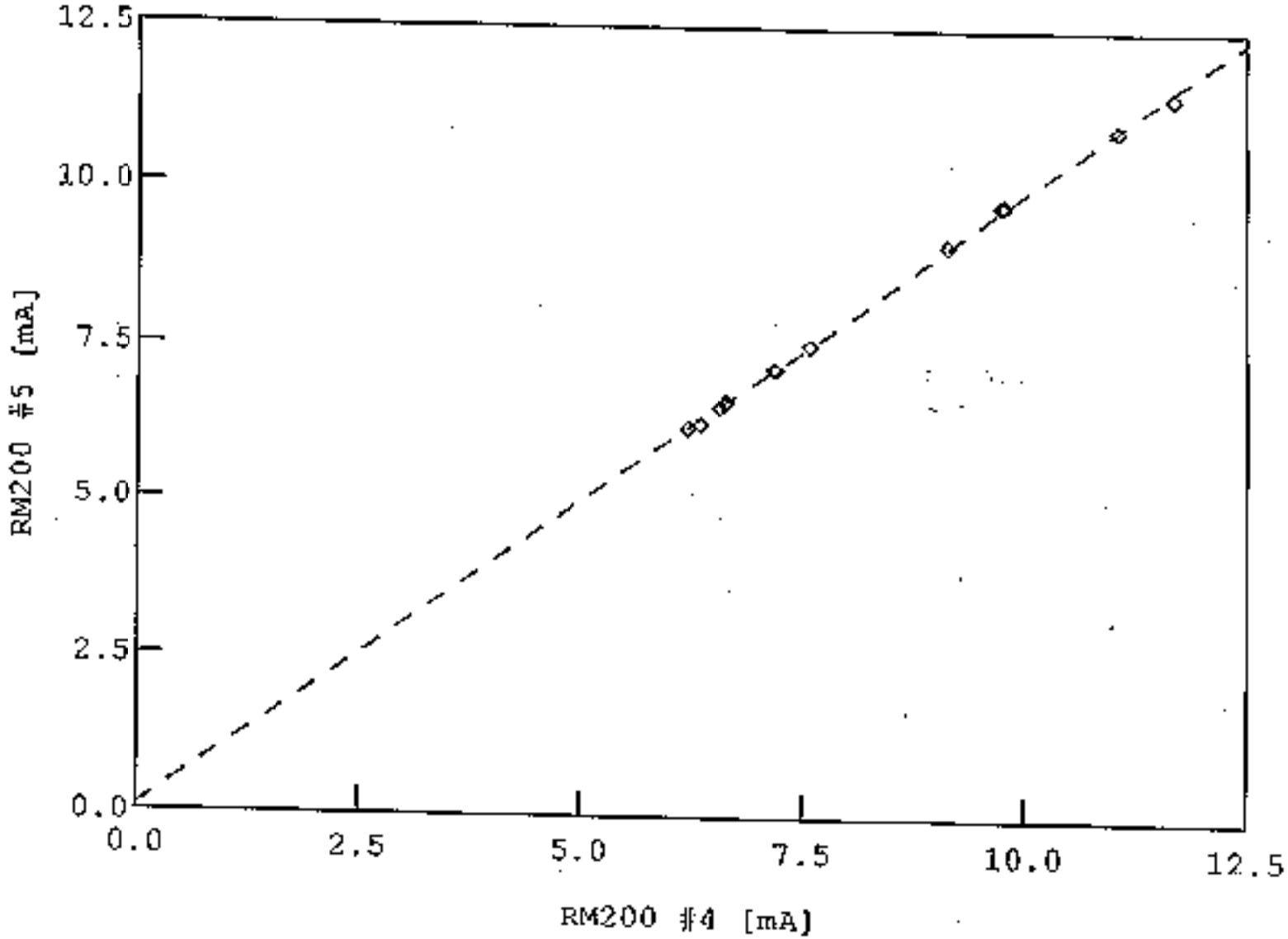

Figure 2-8. Reproducibility of the RM200 measurements.

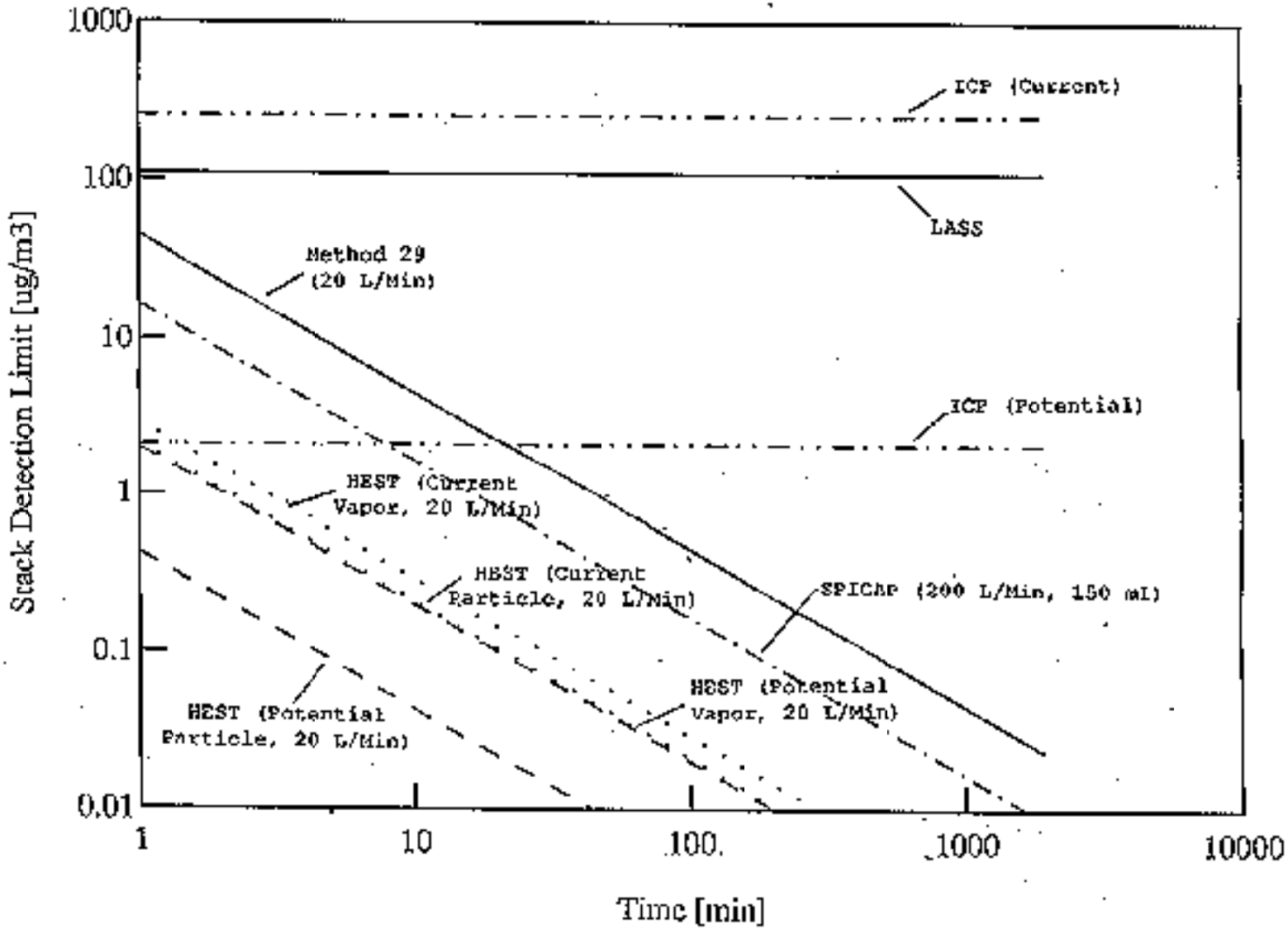

Figure 2-9. Multi-metals CEMs detection limits.

CHAPTER 3

CEMS PERFORMANCE SPECIFICATIONS AND DATA QUALITY ASSURANCE

3.0 INTRODUCTION

EPA has developed CEMS performance specifications for all stack emissions that will be regulated, regardless of whether or not a demonstrated CEMS currently exists. This allows the optional use of CEMS beyond those currently required as the technology becomes available and demonstrated. The CEMS that will be required under the new rule fall into two groups: those that were required under the old rule (O_2, CO, and THC), and those that will be required for the first time (PM and total mercury). The decision to require PM and total mercury CEMS is based on the availability of instruments and EPA's assessment that monitoring using these instruments is feasible, pending the outcome of demonstration tests to be held in 1996.

In general, the performance specifications that have been developed have, for the purposes of consistency, followed the general form and requirements of 40 CFR part 60, Appendix B, Performance Specification 2 for SO_2 and NO_x CEMS (PS 2). In fact, PS 2 has been used as a standard for what is in general the minimum performance acceptable by a CEMS for compliance purposes. These performance specifications contain specifications and test procedures for calibration and zero drift, calibration error (where applicable), interference tests (where applicable), relative accuracy, and response time. Recommendations for location are also included.

All of the performance specifications contain a requirement that the CEMS sample continuously and have a response time less than or equal to two minutes. This is the current requirement for the CEMS required under the BIF rule, and it is adopted in the new rule and performance specifications because hazardous waste burning facilities are characterized by transient changes in their emissions due to the variability of the feed. The objective of this requirement is to ensure that the CEMS can track these emission transients. In the case of batch CEMS this requirement is waived and the following requirements apply. Sampling time must be no longer than one-third of the averaging time. This allows three or more measurements per sampling period, thus providing some warning of an impending violation and allowing time for corrective

action to be taken. A maximum delay of one hour for analysis of the sample is allowed, and the pause in sampling between exchange of sampling media must be less than 5% of the averaging period or 5 minutes, whichever is smaller.

In the sections that follow the various performance specifications are discussed in turn. The performance specifications themselves are included in the appendices in their entirety. Terms used in the performance specifications that require definition are the following. Relative Accuracy (RA): RA is assessed through comparison of a CEMS response to reference method measurements. Both the CEMS and reference method measurements are made in the stack. Calibration Error (CE): CE is assessed by a challenge to the entire CEMS using an NIST traceable calibration standard (equivalent to a cylinder gas audit). Calibration Drift (CD): CD is assessed by a challenge to the analyzer portion of a CEMS using a stable standard.

3.1 PERFORMANCE SPECIFICATIONS

3.1.1 PM

The performance specification for PM CEMS is based on the International Standards Organization (ISO) PM CEMS performance specification, 10155 (ISO 10155). A calibration of the CEMS against manual gravimetric measurements is required, the statistical treatment of the calibration data is specified, and minimum requirements on the quality of the calibration relation are set. These requirements are roughly equivalent to a relative accuracy of 20%. Calibration and zero drift are specified as less than 2% of the emission limit, and span is required to be at least three times the emission limit. Because the PM properties that define the CEMS response may change as operating and load conditions change, the range of validity of the calibration is limited to the PM load range over which the calibration was carried out. Further, recalibration is required if facility operation or hardware is changed.

3.1.2 Mercury

The performance specification for mercury requires a measurement of total mercury, regardless of speciation or phase. The requirement to measure PM bound mercury is included because a regulated facility may use carbon injection for mercury control. In this instance, a significant fraction of the emitted mercury could be adsorbed on carbon particulate that escapes the PM control device.

Calibration of a total mercury CEMS poses a particular challenge because typically these devices use analyzers that detect elemental mercury alone. Sensitivity to speciated mercury is

achieved by using a converter that reduces all speciated mercury to elemental mercury. Thus performance of the converter must be assessed using a source of speciated mercury, typically mercuric chloride, as this is the most important speciated form in terms of emissions. Performance of the analyzer, however, must be assessed using an elemental mercury source. Calibration sources for mercury and mercuric chloride are very difficult to use, however, as the concentration that is generated depends very sensitively on temperature. These compounds also tend to adsorb on and permeate surfaces. For these reasons the calibration requirements and specifications for a total mercury CEMS are unique. The performance specification requires that the daily calibration drift be determined using only a calibration standard for elemental mercury. This simplifies the procedure and checks just the analyzer performance. A more involved procedure, to check the performance of the entire CEMS, is required at installation and at less frequent intervals as specified in the data quality assurance requirements. This procedure evaluates "calibration error", and involves using calibration sources for both elemental mercury and mercuric chloride. In this procedure, the entire CEMS is challenged at three different levels with each source, thus evaluating both analyzer and converter performance.

Because of the difficulty in using the calibration sources, the specifications for a mercury CEMS are looser than for other types of CEMS. Calibration error, evaluated for both elemental mercury and mercuric chloride, is specified as less than 15% of the reference value at levels of 0-20%, 40-60%, and 80-120% of the emission limit. Calibration drift, evaluated for just elemental mercury, is specified as less than 10% of the reference value, and zero drift as less than 5% of the emission limit. Relative accuracy, evaluated against EPA reference methods, is specified as less than 20% of the mean of the reference method test data or 10% of the emission limit, whichever is greater. In addition, an interference test using specified concentrations of CO, CO_2, O_2, SO_2, NO_2, H_2O, HCl, and Cl_2 is required. The sum of the interferences must be less than 10% of the emission limit. Finally, since it is the nature of hazardous waste incinerators that their emissions can vary suddenly and widely, the span of the instrument is specified as twenty times the emission limit.

3.1.3 HCl and Cl_2

The performance specifications for both HCl and Cl_2 require that the CEMS directly measure the gas phase concentration of these two pollutants. This is because CEMS that capture these species in solution and measure the chloride ion, for example, can also respond to chlorine from other sources. Both of these CEMS have similar span (twenty times the emission limit), drift (less than 2.5% of emission limit), accuracy evaluated through calibration error (less than 10% of emission limit), and interference specifications (sum of interferants less than 2% of the emission limit). Accuracy assessed through the calibration error test procedure will be the only evaluation

of accuracy required for these two monitors. The calibration error test procedure is similar to a "cylinder gas audit" (see PS 2) , and is feasible since certified cylinder gases are available for HCl (as EPA protocol 1) and Cl_2 (certified NIST traceable). A relative accuracy test audit (RATA) against the manual EPA reference method 26A is not required because of concerns about the accuracy of the reference method. Method 26A has been shown to have significant biases associated with the presence of other halogens in the stack gas (EER, 1995), and, because the method measures chloride ion concentrations captured in the liquid phase, it is also sensitive to chlorine in forms other than HCl and Cl_2.

3.1.4 Multi-metals

The performance specifications for multi-metals CEMS follow the form and general requirements of PS 2 and the other new performance specifications developed by EPA. Span is specified as twenty times the emission limit, and calibration and zero drift as less than 5% of the emission limit. Relative accuracy, evaluated against EPA reference methods, is specified as less than 20% of the mean of the reference method test data or 10% of the emission limit, whichever is greater. Relative accuracy must be evaluated for every metal at a level above the detection limits of both the CEMS and the reference method. Relative accuracy for one metal must be assessed at three different levels: 0-20% of the emission limit, 40-60% of the emission limit, and 80-120% of the emission limit. Because this requirement means that significant levels of that metal will have to spiked into the system, the option of carrying out this test with iron is allowed. Iron was chosen because it is not a HAP, it is detectable by all of the technologies under development as multi-metal CEMS, and the costs associated with spiking should be lower.

3.1.5 O_2

The performance specification for O_2 CEMS follows 40 CFR part 60, Appendix B, PS 3 very closely. Some changes, taken from 40 CFR part 266 Appendix IX, PS 2.1(BIF rule) have been incorporated. The essential requirements are as follows. Span is specified as 25% O_2, and recorder resolution as 0.5% of span. Calibration and zero drift are specified as less than 0.5% O_2. Relative accuracy is specified as less than 20% of the mean of the reference method measurements or 1% O_2, whichever is greater. Calibration error must be assessed at three ranges, and must be less than 0.5% O_2. And finally, a response time of less than two minutes is required.

3.1.6 CO

The performance specification for CO CEMS follows 40 CFR part 60, Appendix B, PS 4A very closely. Some changes, taken from 40 CFR part 266, Appendix IX, PS 2.1 (BIF rule) have

been incorporated. The essential requirements are as follows. Span is specified for two ranges: low span is 200 ppm, and high span is 3000 ppm. Recorder resolution is specified as 0.5% of span. Calibration and zero drift are specified as less than 3% of span. Relative accuracy is specified as less than 20% of the mean of the reference method measurements or 5% of the emission limit, whichever is greater. Calibration error must be assessed at three ranges, and must be less than 5% of span. And finally, a response time of less than two minutes is required.

3.1.7 Total Hydrocarbon

The performance specification for total hydrocarbon CEMS in 40 CFR part 266, Appendix IX, PS 2.2 will be used.

3.1.8 Summary

The main features of the performance specifications described in the preceding sections are summarized in Table 3-1. Note that calibration error tests rather than RATA's are relied on exclusively to assess accuracy for HCl, Cl_2, and THC CEMS. The use of RATA's is optional for O_2 and CO CEMS. These are all CEMS for which cylinder gases are available. For CEMS where this is not the case, RATA's involving comparison to reference method measurements are required.

3.2 DATA QUALITY ASSURANCE

Terms used in the data quality assurance requirements that require definition are the following. Relative Accuracy Test Audit (RATA): RATA's involve an assessment of a CEMS relative accuracy through comparison to reference method measurements. Both the CEMS and reference method measurements are made in the stack. Absolute Calibration Audit (ACA): an ACA is equivalent to the calibration error tests that are defined in the performance specifications. An ACA uses NIST traceable standards to challenge the entire CEMS (introduced as close to the sampling nozzle as possible) in order to assess accuracy. Response Calibration Audit (RCA): for PM CEMS only, this is a check of the stability of the calibration relation, performed by comparison of the CEMS response to manual gravimetric measurements.

The basic structure of the data quality assurance requirements is the same as Appendix F of 40 CFR part 60. Daily calibration and zero drift checks are required. Data accuracy for PM CEMS is assessed by quarterly ACA's at three levels and approximately yearly RCA's. Data accuracy for multi-metal and mercury CEMS, because of the costs of carrying out the tests, is assessed by quarterly ACA's and RATA's every three years, to coincide with comprehensive

testing of the facility (large facilities will be tested every 3 years, and small ones every 5 years). Data accuracy for all other CEMS will be assessed by quarterly ACA's and yearly RATA's (except for PM, which will be on a schedule of testing at twice the frequency of comprehensive tests: every 18 months for large facilities and 30 months for small facilities). This is summarized in Table 3-1.

3.3 AVERAGING PERIODS

For compliance purposes the CEMS data are averaged over a specified period of time and then compared to the emission limit. Since the emission limits are based on CoC data obtained using EPA manual method measurements, it is the length of time taken to make these measurements that defines the averaging time. Averaging times shorter than this can not be used because there is no data about the behavior of the sources on time scales shorter than the time taken to obtain the CoC data. The averaging times determined from the EPA database for each CEMS are summarized in Table 3-2.

TABLE 3-1. SUMMARY OF CEMS PERFORMANCE SPECIFICATIONS/DATA QUALITY ASSURANCE REQUIREMENTS

CEMS	Comments	Span	CD/ZD	RA	CE	Interference	DQA
PM	Site-specific calibration	3X limit	<2% of limit	<20% at limit	None	None	RCA every 1.5 years/ ACA yearly
Hg	Total (including PM bound)	20X limit	<10%/ <5% of limit	<20% of RM <10% of limit	3 levels <15% of ref	<10% of limit	RATA every 3 years/ ACA quarterly
Cl2	Gas-phase Cl2	20X limit	<2% of limit	None	3 levels <15% of ref	<2% of limit	RATA yearly/ ACA quarterly
O2		25%	<0.5% from ref	<20% of RM <1% O2 (optional)	3 levels <0.5% O2	None	RATA yearly/ ACA quarterly
CO		200 pm, 3000 ppm	<3% of span	<10% of RM <5% of limit (optional)	3 levels <5% of span	None	RATA yearly/ ACA quarterly
THC		100 ppm	<3% of span	None	3 levels <5% of span	None	RATA yearly/ ACA quarterly
HCl	Gas-phase HCl	Not specified	<2.5% of span	None	<15% of ref	<2% of limit	RATA yearly/ ACA quarterly
Metals		20X limit	<5% of limit	<20% of RM <10% of limit	None	None	RATA every 3 years/ ACA yearly

TABLE 3-2. AVERAGING TIMES

CEMS	Averaging Time
PM	9 hours
Hg	12 hours
Metals	12 hours
HCl/Cl_2	9 hours
O_2/CO/THC	1 hour (based on CEMS data)

CHAPTER 4

CEMS TESTING

4.0 INTRODUCTION

EPA CEMS testing has proceeded in two phases. Phase I, or "preliminary" demonstration testing, has taken place in conjunction with EPA testing designed to evaluate pollution control equipment. CEMS testing has been incorporated where the opportunity has arisen, defined by whether or not the appropriate reference method measurements are made, whether or not space is available at the site, and whether or not the site is willing to accommodate the CEMS. In addition, vendors have been asked on short notice to participate. The aim of this testing has been to find out whether or not fieldable instruments are available, and to obtain an initial indication of their performance. This has been accomplished by making limited comparisons with manual reference method measurements and by allowing the CEMS to operate anywhere from one to six weeks.

Phase II will consist of formal demonstration testing designed to evaluate the CEMS in terms of all of the requirements in the draft performance specifications. The objective will be to establish that there is at least one unit available that can meet the performance specifications, and hence be used for compliance monitoring. Since only two new CEMS would be required, these are the only two types which will be tested. These are CEMS for PM and total mercury. Participation in the program will be solicited by a request for proposals published in the Federal Register and in the Commerce Business Daily. Selection of participants will be made by scoring the proposals against a set of selection criteria.

Phase I testing, both completed, ongoing, and planned, is described in sections 4.2, 4.3, and 4.4. The Phase II demonstration program is described in section 4.5.

4.1 TESTING AT ROLLINS BRIDGEPORT FACILITY

4.1.1 Introduction

Three PM CEMS were evaluated downstream of a pilot scale wet ESP installed at the Rollins Environmental Services commercial hazardous waste incinerator in Bridgeport, NJ (EER, 1995a). The CEMS were chosen to represent three different measurement approaches: light scattering, time dependent optical attenuation, and the beta gauge. The tests were carried out in March of 1995, and were performed in three stages. First, the CEMS were calibrated according to ISO 10155 using manual gravimetric measurements (EPA Method 5). Second, the CEMS were allowed to operate for a period of about two weeks. And finally, additional manual method measurements were made in order to check the stability of the original calibration.

4.1.2 Description of the Test Site

The test site chosen was the Rollins Environmental Services hazardous waste incinerator in Bridgeport, NJ. This facility is a commercial incinerator that burns a mix of solid and liquid hazardous waste in a rotary kiln equipped with an afterburner. The flue gases are treated by an emission control system consisting of, in order, a saturator (rapid quench), packed tower absorber, high-energy venturi scrubber, and a mist eliminator. The resulting PM emissions from this system are typically in the 20 mg/m^3 range. During the PM CEMS evaluation a slipstream of flue gases taken downstream of the induced draft (ID) fans and the emissions control system described above was treated by a pilot scale wet electrostatic precipitator (WESP), which dropped the PM emissions to the 1 mg/m^3 level. The PM CEMS were located downstream of the WESP but before the slipstream was returned to the main duct at a point upstream of the ID fans (Fig. 4-1). The slipstream duct diameter was 30.5 cm, and consisted of sections of both flexible plastic and hard fiberglass ducting, the latter fitted with flanges for sampling and access for the CEMS. The flue gases at the measurement point were saturated at a temperature of about 24 C. Previous measurements showed that the particles were predominantly less than 10 µm, and a substantial fraction (50 to 80 percent) were less than 1 µm. The presence of liquid aerosol was also a possibility due to both the operation of the WESP and the venturi scrubber, and the low temperature, saturated nature of the flue gases. Because of the high variability of the waste burned, the characteristics of the PM produced were also expected to be unusually variable, and hence to provide a demanding challenge to the PM CEMS.

4.1.3 Description of the PM CEMS

The three PM CEMS chosen represented measurement approaches based on light scattering, time-dependent optical attenuation, and beta particle transmission (beta gauge). Both optical approaches require site specific calibration in order to relate instrument response to PM mass loading. The beta gauge response is basically independent of the properties of the particulate, and thus a universal calibration is provided by the manufacturer (site specific calibration is not necessary). However, the beta gauge is an extractive system, and is heated to prevent interference due to water and to ensure a measurement of dry particulate. Thus the beta gauge was tested in order to evaluate the possible biases associated with the accuracy of the calibration, losses in the sampling system, and the effectiveness of the heating system.

The light scattering device tested was the Sick RM200. This device measures the light scattered at approximately 90 degrees by the particulate. The light beam is generated by a near infrared LED (880 nm), and the sample volume is about 100 cm^3 located 12 cm from the wall. Both the light source and the detector are located in a single unit thus requiring only one point of access to the duct. The RM200 is designed to carry out automatic zero and span checks, and provides automatic compensation for dirt on the optics (although the optics are protected by an air purge system). The RM200 is normally located directly on the duct wall, thus making an in-situ measurement. However, for application on low temperature wet systems such as the Rollins facility, the RM200 is used with a hot bypass system. A slipstream was extracted from the duct, passed through a cyclone heater, and then passed through the sample volume of the RM200. The slipstream was then returned to duct. This system ensured the measurement of dry particulate only.

The time dependent optical transmission device tested was the BHA Group Inc. CPM1000™. This device measures the fluctuations in transmitted intensity of a light beam passed across the duct. The light source is a modulated LED, which allows a constant sensitivity to be maintained by adjusting the source intensity to maintain constant detector output at the modulation frequency, thus compensating for aging of the source and dirt on the windows. The CEMS response is generated by using the AC coupled output from the photo-detector, therefore the instrument responds to moving particulate only, not to changes in the DC level of the transmitted intensity, as in opacity monitors. This difference between monitoring opacity and time dependent transmission accounts for the much greater sensitivity of the latter, which can be used down to PM loadings of 0.1 mg/m^3. As the CPM1000™ was mounted directly on the duct, its response was not necessarily proportional to dry particulate, but rather to particulate at stack conditions and to any liquid aerosol that might have been present.

The beta gauge device tested was the Emissions SA Beta 5M. This device uses a heated sampling probe to obtain an isokinetic sample (isokinetic sampling is maintained automatically). The sample is collected on a filter, which, at the end of the sampling period, is moved (using a continuous filter tape mechanism) to a measurement location between a carbon 14 beta particle source and a detector. The beta transmission through each blank filter is determined before sampling begins. The sampling duration is programmable and determines the mass concentration detection limit. At high PM loadings it must be kept small enough to prevent sampling excessive amounts of particulate, and is usually set at two minutes for typical applications. Analysis takes six minutes, and thus a measurement is made every eight minutes (these settings were used for the testing described here). At the end of each sampling period, the probe nozzle is temporarily closed, opened, and closed again in order to reentrain any particulate that may have deposited in the probe.

The RM200 and Beta 5M were installed and commissioned by technicians from Sick and Emissions SA respectively. The CPM1000™ was installed and commissioned by personnel from Energy and Environmental Research (EER) and Rollins. The analog output from each device was connected to an A/D and logged on a computer using Labtech Notebook. The CEMS outputs were sampled every second, and 1 minute averages were calculated and stored.

4.1.4 Experimental Procedure

The CEMS were all operated simultaneously and continuously during the regular daytime shift (about 8 hrs per day). During the manual method runs the hours of operation were extended as necessary. The initial comparisons were conducted by making simultaneous manual method measurements at a point upstream of the CEMS (and downstream of the WESP). The measurements were made using EPA Method 5. The Method 5 runs were made in duplicate, with two sampling trains simultaneously traversing the duct through 2 ports set at 90 degrees to each other. The entire layout for the test is shown in Figure 4-1. Three runs were made at each of three conditions designed to produce different PM loadings, for a total of nine sets of paired manual method and CEMS data. The three different conditions were obtained by varying the WESP voltage, and were 1) WESP off, 2) WESP on at a low voltage (46, 48, and 52 KV), and 3) WESP on at high voltage (52 to 53 KV). No other manipulation of facility operation was made, and other than these changes to the slipstream conditions the plant operated normally during the test period.

The initial comparison measurements took place over a period of four days, and only the RM200 and CPM1000™ were in place. Over the next two weeks, exclusive of an unscheduled plant shut down, 9 days of CEMS data were obtained. The Beta 5M was online

for this period. During the final two days of the test period additional manual method measurements were made in order to re-check the relationship between the CEMS responses and the manual gravimetric measurements. These additional measurements consisted of four sets of runs at two conditions: low (46 KV) and high (52 KV) ESP voltage.

The calibration calculations were carried out following the procedures given in ISO 10155. Briefly, these involve performing a regression analysis on the paired CEMS and manual method data. A 95% confidence interval for the regression relation is also computed, as is a tolerance interval bounding 75% of the population of the paired CEMS and manual method data with 95% confidence. In essence, the confidence interval gives the 95% confidence on the uncertainty of the PM loading calculated from the CEMS response using the regression relation, while the tolerance interval bounds the region within which one would expect continued paired CEMS and manual method measurements to fall (based on the measurement pairs used to perform the calibration). Subsequent measurements comparing the CEMS response to the manual method are consistent with the calibration relation if at least 75% of them fall within the tolerance interval.

4.1.5 Results and Analysis

The manual method measurements against which the CEMS were compared were performed over a period of four days with the WESP operated at high voltage, low voltage, and turned off. The durations of the manual method runs were the following: 1 hour for the ESP off condition, 3 hours for the low voltage condition, and four hours for the high voltage condition. The high voltage condition resulted in PM loadings around the 1 mg/m^3 level, while with the ESP off the PM loading was about 20 mg/m^3. At the lower PM loadings most of the particulate catch was in the probe rinse. The results from these measurements, and those from the four additional sets of measurements performed at the end of the test period, are summarized in Table 4-1. Table 4-1 also includes the outputs from the RM200 and CPM1000™ averaged over the durations of the manual method runs. The manual method measurements reported in Table 4-1 are on a dry basis, corrected to 20 C, and uncorrected for oxygen.

During the first set of manual method measurements it was noted that when the sampling ports were opened in order to traverse the probes that the inflow of cold, 3 C air (the ducting was under negative pressure) coincided with an elevated response from the CPM1000™. This was due to condensation, which gave rise to an increase in liquid aerosol in the duct. As discussed previously, the CPM1000™ was sensitive to liquid aerosol as well as dry particulate since it was making a direct, in-situ measurement. For this reason, we believe that at the low particulate levels found downstream of the operating WESP that the

bulk of the response from the CPM1000™ was due to liquid aerosol that was always present. Two additional pieces of data support this conjecture. First, there was a continual buildup of liquid water at low points in the ducting. Thus it was quite likely that gas phase condensation was occurring as the gas stream cooled during its passage through the duct. Second, the CEMS data record during a failure of the plant's solids shredder, shown in Figure 4-2, shows no decrease in PM levels detected by the CPM1000™. The failure occurred at about minute 66 in the graph shown in Figure 4-2, and was detected by the RM200 (which was configured to respond to dry particulate only). Thus a calibration of the CPM1000™ based on the data in Table 4-1 forces the low level output of the CPM1000™ due to the liquid aerosol to agree with the manual method measurements at that level. Recognizing this fact, a calibration relation (Fig. 4-3) was derived for the CPM1000™ from the data in Table 4-1 (the averages of the manual method measurements were taken as the reference method values for each of the 8 measurement points used in the calibration) and used to convert the CPM1000™ output to PM loading.

The calibration relation for the RM200 is shown in Figures 4-4 and 4-5. The dashed line in Figure 4-4 represents the calibration relation, the inner pair of solid lines surrounding the calibration relation are the confidence interval on the calibration relation, and the outer pair of solid lines are the tolerance interval. The data points from the initial calibration are shown as diamonds, while the data points from the calibration check are plotted as triangles. The same information is rescaled and presented in Figure 4-5 also, since the bulk of the data falls at such low values in Figure 4-4. This calibration is based on the same eight data pairs as used for the calibration of CPM1000™, for which one data point was lost because the output went off the recording scale. The confidence interval of the calibration is 13% at the 20 mg/m^3 level and 91% at the 1.5 mg/m^3 level. Note that the measurements from the calibration check fall within the tolerance interval of the calibration, which is 19% at the 20 mg/m^3 level and 220% at the 1.5 mg/m^3 level. Since the calibration check was performed at the 1.5 mg/m^3 level, any result within a factor of 2.2 would indicate agreement, and thus, with such a large uncertainty associated with the data set, this is not a very conclusive test. This is due in part to the high variability of the manual method measurements. The average relative standard deviation of the paired data is 19%. Using the differences between the duplicate runs as the basis for a calculation of the scatter of the data using the same equations as used to calculate the confidence interval reveals that the precision of the manual method measurements accounts for roughly half of the magnitude of the confidence interval.

A record of the CEMS outputs for the extended test period following the first manual method comparisons is shown in Figure 4-6 (the periods when the CEMS and the WESP were off have been deleted from the graph). The calibrations derived from the manual method data were used to convert the RM200 and CPM1000™ responses to mg/m^3, which

forces rough agreement between these two CEMS at the 1.5 mg/m^3 level. The Beta 5M output is directly in mg/m^3. The PM levels for most of the test period were near the detection limit of the Beta 5M (1.25 mg/m^3 based on a sampling time of two minutes), and thus its output for the bulk of the test period is essentially non-detect. Since the only high emissions condition during which manual measurements were made occurred during the initial calibration period, no comparison between the Beta 5M and the manual measurements was possible.

Inspection of the CEMS record in Figure 4-6 shows that there was one occasion when both the CPM1000™ and RM200 saw high emissions. On that occasion the Beta 5M reported 5.8 and 4.6 mg/m^3 for two periods during the high emissions, compared to a reading of 4.0 mg/m^3 from the CPM1000™ (the RM200 went off scale). Why the Beta 5M did not report at that level for the entire duration of the elevated emissions is unknown. There were also two occasions where the CPM1000™ showed an extended period of significantly higher PM emissions that neither the RM200 nor the Beta 5M indicated. Finally, the spikes that can be seen in the RM200 data shown in Figure 4-6 can be associated in every instance with flushing (which is accompanied by turning off the ESP field for a few minutes) or shutdown of the WESP.

4.1.6 Discussion and Conclusions

The ISO PM CEMS performance specifications call for a confidence interval of less than 10% and a tolerance interval of less than 25% at the emission limit level, and a correlation coefficient of greater than 0.95. If we assume a hypothetical emission limit equal to the upper end of the calibration range of 20 mg/m^3 measured in this work, then the RM200 was very close to meeting these specifications despite several deficiencies in the data that contributed to the fairly large confidence and tolerance intervals. These were the following. First, the low WESP voltage condition did not produce a PM loading sufficiently different from the high voltage condition. The result was that the calibration was based on two very widely spaced clusters of points. This contributed to both the very good correlation coefficient and the large confidence and tolerance intervals. Second, the very low PM loadings were difficult to measure using the manual method. Longer sampling times would improve the precision of the manual measurements (which was estimated to be responsible for half of the magnitude of the confidence interval), and thus improve the uncertainty in the calibration relations. Finally, nine data points is the minimum number that should be used for determining the calibration relation following the ISO performance specification procedure (in Germany at least 15 data points are recommended), rather than the eight points used here. Noting that it is dangerous to attach too much weight to the calibration and its associated confidence and tolerance intervals calculated here given these limitations associated with the current data set, the results obtained in this study suggest that the RM200 can be successfully

calibrated under these conditions (ie, meet the performance specifications) provided that more extensive and precise manual measurements are made.

During most of the test period the RM200 and CPM1000™ were in general agreement (based on the calibrations with their associated limitations as discussed in the previous section). As noted earlier, there were two instances of rather large and extended disagreement. While the cause of this discrepancy is unknown, a possible explanation lies in the difference between the installation of the two CEMS. The RM200 was configured to withdraw and dry a slipstream of stack gas, thus measuring dry particulate, while the CPM1000™ was installed directly on the duct. Any liquid aerosol present would thus have contributed to the signal from the CPM1000™, but not to that from the RM200. It is therefore likely that the high readings by the CPM1000™ were caused by a leak in the ducting giving rise to higher liquid aerosol levels. The fact that the RM200 continued to respond to the WESP flushing procedure, and that neither the RM200 nor the Beta 5M saw the elevated emissions reported by the CPM1000™ (although the Beta 5M did see the high emissions when they were indicated by both the CPM1000™ and RM200), suggest that the RM200 output was indicative of the true dry PM emissions during those periods under discussion. This is further supported by the response of the RM200 when the plant stopped burning solids (see Fig. 4-2), an event which one would expect to be associated with lower PM emissions. These results indicate that it is necessary to extract and dry a slipstream in order to obtain accurate dry PM measurements, rather than the existence of any problem with the measurement principle of the CPM1000™ itself.

The Beta 5M output was consistent with the PM levels indicated by the other CEMS (as discussed previously). The intermittent non-zero readings that can be seen in Figure 4-6 are what one would expect from an instrument operated right at its detection limit, and during the period of high emissions detected by all three instruments the output of the Beta 5M was in rough agreement (+30%) with the CPM1000™. However, insufficient data was obtained to properly evaluate the performance of the Beta 5M.

In conclusion, the calibration data did not meet minimum requirements for 1) three or more different ranges of particulate loading and 2) nine or more data points. However, the results that were obtained suggest that with proper care an optical device used in conjunction with a hot bypass can be calibrated at this facility in conformance with the ISO performance specification for particulate monitors. The check on the stability of the calibration relation for the optical device was inconclusive due to the very low particulate levels at the test condition. The behavior of the three CEMS over the two week test period indicated that, for a low temperature, saturated stack gas, it is appropriate to extract and dry a slipstream rather than

attempting to make an in-situ measurement. The results obtained with the beta gauge device were inconclusive, although its behavior was consistent with the other CEMS. Finally, it should be noted that all three devices functioned properly over the two week test period with no operator intervention.

4.2 TESTING AT THE LAFARGE FREEDONIA FACILITY

The phase I testing at the Lafarge Cement Co. plant in Freedonia, KS evaluated the following CEMS. For PM: the Sick RM200 and the ESC P5A, both light scattering devices. For total mercury: the Verewa total mercury monitor. For PAH: the EcoChem PAH monitor. And for PIC's: the EcoLogic CIMS-500 mass spectrometer system made by V&F. The Lafarge facility at Freedonia has an APCS consisting of an ESP. Temperature and PM loading at the sampling location in the duct immediately downstream of the ESP (upstream of the ID fan and stack) are approximately 350 F and 0.02 gr/dscf, respectively.

The field phase of this program has been completed. Preliminary analysis of the PM data indicates a stable calibration relation over a period of 8 weeks which met the performance specifications. Figure 4-7 shows the calibration relation (dashed line), confidence interval (inner pair of solid lines), and tolerance interval (outer pair of solid lines) for the initial calibration of the ESC P5A (diamonds). Subsequent calibration data taken over an eight week span are shown as squares and crosses. With the exception of the three data points at the low ESP voltage condition (lower right) from calibration 3, which indicate lower PM levels than at the mid voltage condition according to the manual method measurements (and which are suspected to be innaccurate), all of the data falls within the tolerance interval.

The manual method data for the mercury and organics measurements is not yet available with which to evaluate the other CEMS. However, at this point the following is known. The mass spectrometer system was late in arriving and was damaged during shipment. Although EcoLogic was able to eventually make measurements, they were not concurrent with the reference method measurements, and thus comparison will not be conclusive. In addition, due to the damage to the instrument the measurements were not stable. The PAH monitor was unable to make any measurements at all due to the location of the sampling point downstream of the ESP. This effect was due to the residual charge in the flue gas generated by the ESP. This charge interferes with the physics of the measurement.

4.3 TESTING AT THE MEDUSA WAMPUM FACILITY

Testing at the Medusa Cement Co. facility in Wampum, PA, which was discussed in earlier drafts of this document, will probably not take place.

4.4 DEMONSTRATION TEST PROGRAM

EPA plans to hold a demonstration of PM and total mercury CEMS for stack monitoring at hazardous waste burning facilities. The purpose of the demonstration is to 1) determine whether or not CEMS for PM and total mercury are available that can meet the performance specifications proposed as part of the proposed rule "Standards for Hazardous Waste Combustors," and 2) demonstrate long term endurance over a period of 6 months to one year. The proposed performance specifications contain requirements for:

1) a 1 week calibration and zero drift check,
2) relative accuracy assessment against EPA manual reference methods,
3) a calibration error check (if applicable),
4) an interference test (if applicable),
5) demonstration to the EPA that other requirements, such as response time and data recorder scale, are met.

The participating CEMS will be evaluated to determine if they meet the performance specifications in each one of these areas.

The basis of the program will be the following:

1) participating vendors shall supply, install and operate the CEMS at no charge.
2) EPA will select the participants based on their proposals (against the selection criteria set out below).
3) EPA will select the site and provide site coordination and oversight.
4) EPA will provide for manual method reference measurements.
5) the vendors will conduct all other aspects of the CEMS demonstration (as detailed above) under EPA oversight.
6) all data will be provided to EPA,
7) One CEMS of each type (PM and total mercury) that participates in the demonstration will be selected for the long term endurance test.

The testing is expected to start in January of 1996. Proposals from vendors of PM and total mercury CEMS who wish to participate will be solicited through a request for proposal announcement appearing in the Federal Register and Commerce Business Daily. The proposals will be due six weeks later, and must contain the following:

1) a detailed description of the CEMS and its measurement principle,
2) the performance specifications of the device,

3) a detailed description of the calibration procedure(s) and standards,
4) vendor generated test data bearing on CEMS performance/calibration,
5) extant field data demonstrating performance,
6) a statement that the vendor accepts the basis of the program as outlined above, and a description of how the vendor will meet the vendor responsibilities outlined above.

After preliminary selection, vendors will be given site specific information and must then submit a site specific plan for installation. This plan should include details such as, for example, the strategy to be used for handling the problem of liquid aerosol if the site uses a low temperature, wet air pollution control system and maintenance of adequate purge air and temperature to prevent fouling of the optics or optical access, if applicable. In other words, all measures should be described and taken as if the facility chosen were itself buying the CEMS. Based on these plans a final selection of participants will be made.

The following selection criteria are proposed to serve as guidelines for choosing CEMS to participate in the demonstration and endurance tests. Each CEMS will be scored on a scale of 1 to 10 on each criterion (10 being the best score), and a total score calculated using the weighting factors indicated in brackets. Starting from the highest scoring CEMS and working down, as many CEMS will be selected for participation as possible commensurate with the resources available and the capacity of the test site to reasonably accommodate the CEMS.

1) The CEMS must be commercially available. This should be documented by product literature, a list of installation locations, and references. A CEMS that has an installation and formal testing record will receive a graded score up to the highest score for 100+ installations and successful field demonstration. One that is available as a prototype only, with no firm commercialization plans in place that would lead to availability within the year will receive the lowest score. [**25%**]

2) The CEMS must be provided, installed, and operated by the vendor at no charge to the government. It is expected that the vendor will have personnel stay on-site to run the CEMS, carry out CD and ZD checks if needed, perform the CE check (if applicable), monitor CEMS performance during RA testing, and provide any trouble shooting or maintenance that may be required. It is also expected that all data will be recorded and copies provided to EPA at the test site and at no charge: CD and ZD checks (if automatic adjustments are made the CD or ZD before adjustment or the amount of adjustment must be recorded), CE tests, RA tests, and interference checks. Willingness to guarantee all of the above will receive the highest score, none of the above the lowest score. [**25%**]

3) Documentation supplied by the vendor in the proposal must provide an indication that the CEMS can be expected to meet the performance specifications for CD, ZD, CE, RA, interferences, recorder scale, and response time. Since the proposed emission limits for PM and Hg are 69 mg/dscm and 50 µg/dscm respectively, recorder scale (and span) should be 207 mg/dscm and 1,000 µg/dscm respectively. Ability to meet all of the specifications will receive the highest score, ability to meet none of the specifications will receive the lowest score. [**25%**]

4) The CEMS must have detection limits appropriate relative to the proposed emission limit: 69 mg/dscm for PM and 50 µg/dscm for mercury). Thus detection limits would be expected to be at least one-tenth the emission limit to allow the CEMS to meet CE and RA requirements (< 7 mg/dscm for PM and < 5 µg/dscm for Hg). Ability to meet this specification will receive the highest score, inability to meet it will receive the lowest score. [**10%**]

5) EPA defines a CEMS as sampling the stack gas continuously and making measurements every 15 seconds. EPA also requires the reporting of rolling one minute averages and rolling sixty minute averages. In order to have the potential for acceptance for participation in this demonstration, a CEMS must meet these sampling, measurement frequency, and recording requirements. Thus no score. This criterion must be met.

6) The CEMS design (as evaluated from information supplied in the proposal: description of CEMS and measurement principle and/or supplied test data) should be appropriate relative to the requirements of the performance specification and the application to monitoring stack emissions from hazardous waste combustion. For PM CEMS this means:

I) The CEMS should be maximally sensitive to PM in the 0.1 to 10 µm size range.

ii) The CEMS should not be sensitive to liquid water aerosol

For Hg CEMS this means:

I) The CEMS vendor must have demonstrated at least the ability of the CEMS to detect vapor phase Hg, Hg on PM, and HgCl2.

ii) No interferences (see performance specification). [**15%**]

The proposed installation described in the test plan (this occurs after initial acceptance of the proposal) must be appropriate relative to the requirements of the performance

specification and the application to monitoring stack emissions from hazardous waste combustion. Namely, factors such as flue gas conditions (whether it is a saturated low temperature stream, for example) and purge requirements (flow rate and temperature to ensure that optics and access are not fouled) should be taken into account in the installation. If the proposed installation is not judged by EPA to be appropriate, revision of the test plan may be required. If the vendor is unwilling to make the requested changes, that CEMS may be dropped from the test program (either party may drop out at any time).

Selection for the long term endurance test will be based on: I) willingness of the vendor to participate, ii) performance of the CEMS during the demonstration test in terms of ability to meet the performance specifications [**75%**], and iii) maintenance requirements based on vendor information and experience gained during the demonstration test [**25%**].

TABLE 4-1. SUMMARY OF MANUAL METHOD AND CEMS MEASUREMENTS

Run	Condition (ESP Operation)	Train 1 [mg/m3]	Train 2 [mg/m3]	RM200 [Arb. Units]	CPM1000™ [Arb. Units]
1	Off	17.30	18.67	59.68	29.15
2	Off	19.32	17.34	47.04	32.6
3	Off	36.42	26.94	66.56	
4	Low	2.29	1.88	3.5	1.43
5	Low	3.29	2.18	2.88	4.16
6	Low	0.80	1.63	2.02	3.42
7	High	1.07	0.69	1.49	2.72
8	High	0.91	1.05	1.77	1.8
9	High	0.97	1.06	1.54	2.16
10	High	0.52	1.06	1.58	2.11
11	High	0.53	0.58	1.50	
12	Low	0.86	0.74	2.92	2.02
13	Low	0.57	0.49	2.98	2.02

FIGURE CAPTIONS

Figure 4-1. Schematic of test site.

Slipstream and measurement locations for the CEMS and manual method measurements are shown.

Figure 4-2. Data record for the RM200 and CPM1000™ during upset of solids feed to the plant.

Plant solids shredder failed at about minute 66, resulting in reduction of solids feed to the kiln.

Figure 4-3. Calibration of the CPM1000™.

The paired manual method and CPM1000™ data used to calculate the calibration relation are shown as diamonds. The dashed line is the calibration relation obtained by performing a linear least-squares regression.

Figure 4-4. Calibration of the RM200.

The paired manual method and RM200 data used to calculate the calibration relation are shown as diamonds. The dashed line is the calibration relation obtained by performing a linear least-squares regression. The inner solid lines surrounding the calibration relation show the confidence interval, and the outer pair show the tolerance interval. The data from the calibration check are shown as triangles.

Figure 4-5. Calibration of the RM200 rescaled to show the low level data.

The dashed line is the calibration relation and the solid lines denote the confidence interval. The tolerance interval is outside the range of the graph.

Figure 4-6. Record of CEMS readings for the entire test period.

The CEMS readings have been converted to mg/m^3 using the calibration relations. Note the spikes in the RM200 data, which occur during WESP cleaning and shutdown.

Figure 4-7. Calibration of ESC P5A.

This figure shows the calibration relation (dashed line) derived from the initial calibration data (diamonds). The inner solid lines are the 95% confidence interval on the calibration relation, and the outer solid lines are the tolerance interval. The data from the calibrations 2 and 3 are shown as squares and crosses, respectively.

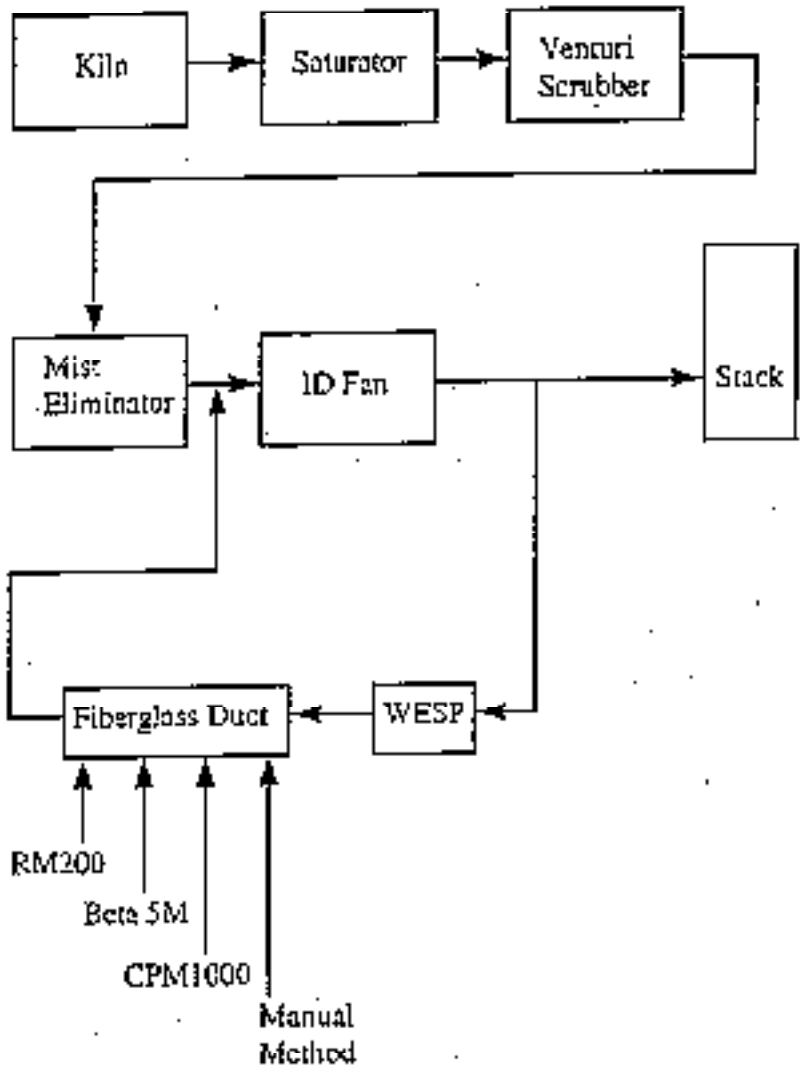

Figure 4-1. Schematic of test site.

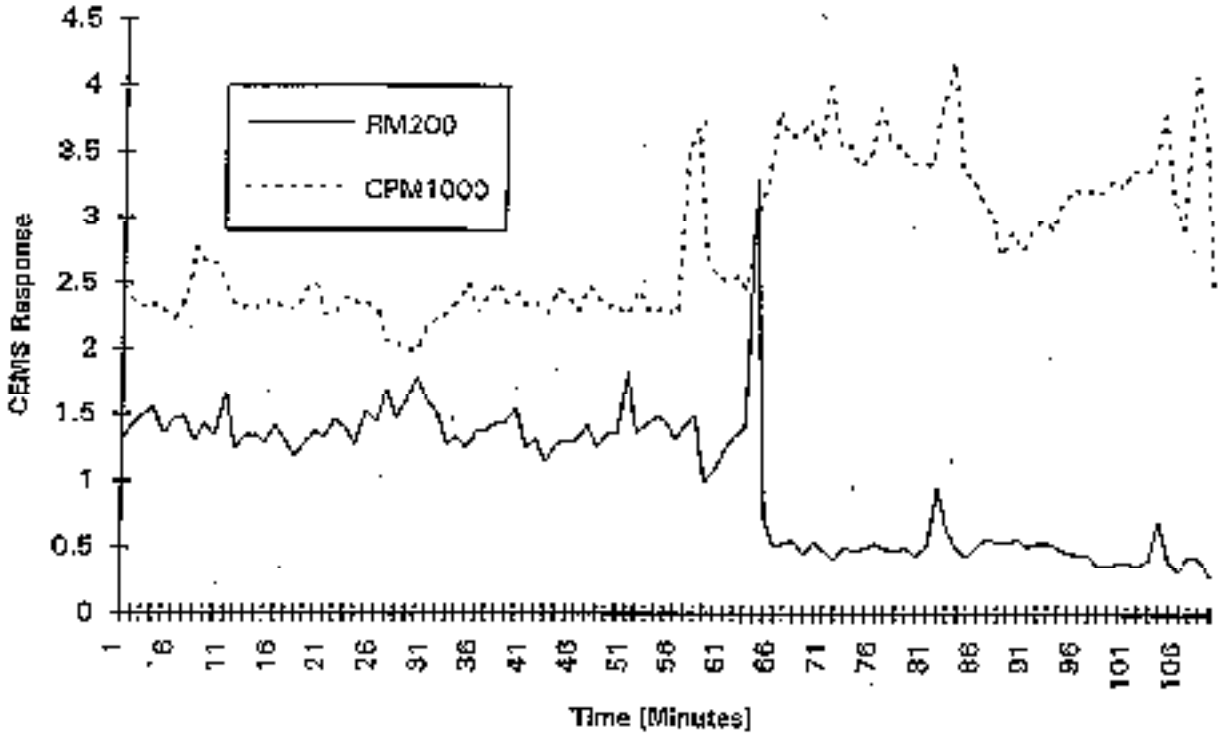

Figure 4-2. Data record for the RM200 and CPM1000™ during upset of solids feed to the plant.

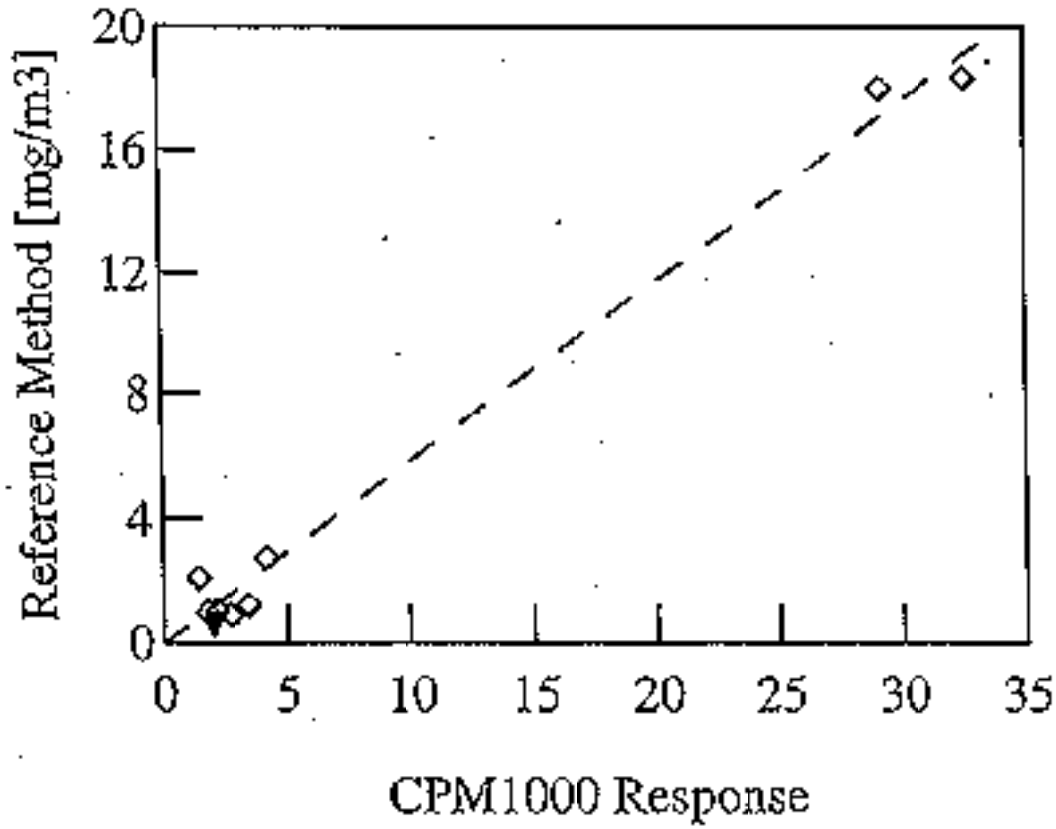

Figure 4-3. Calibration of the CPM1000™.

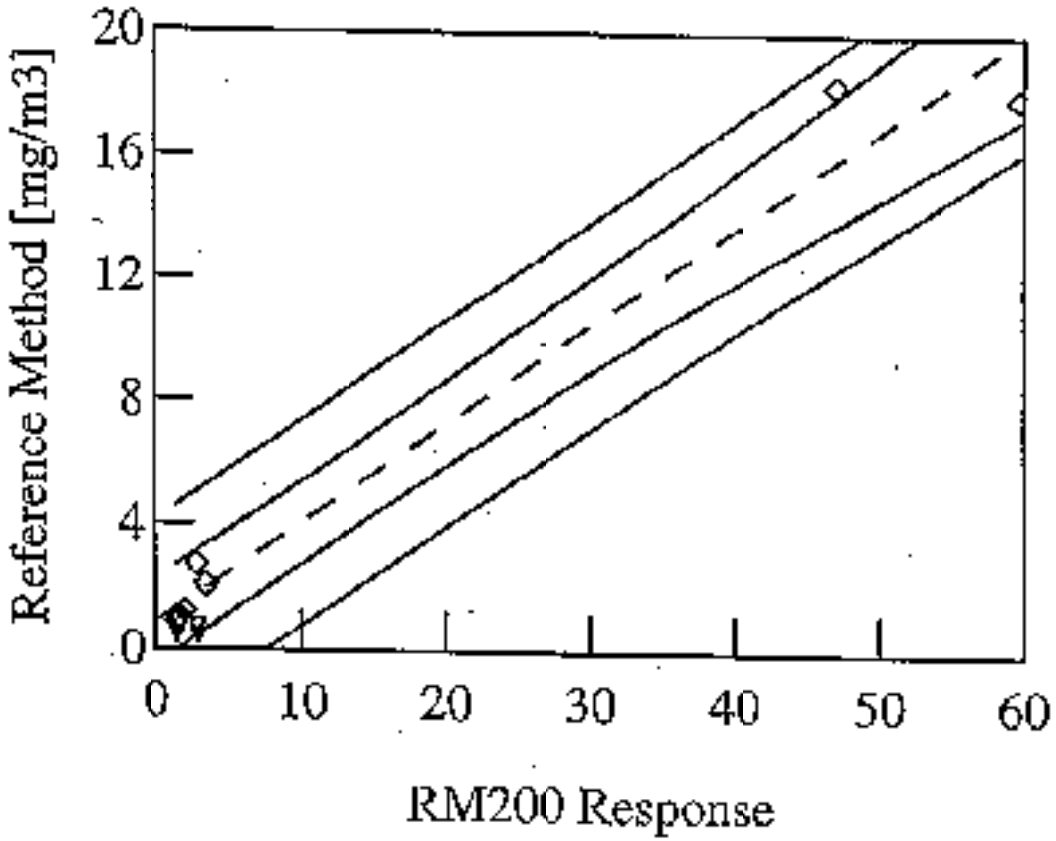

Figure 4-4. Calibration of the RM200.

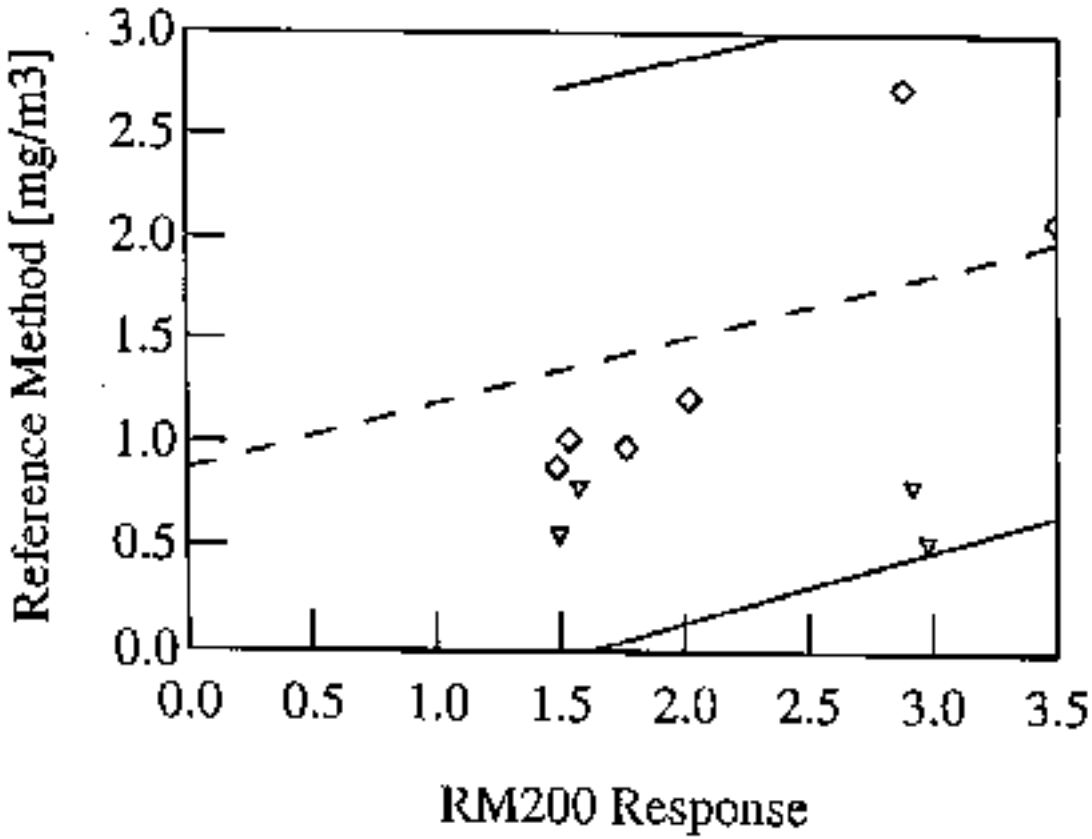

Figure 4-5. Calibration of the RM200 rescaled to show the low level data.

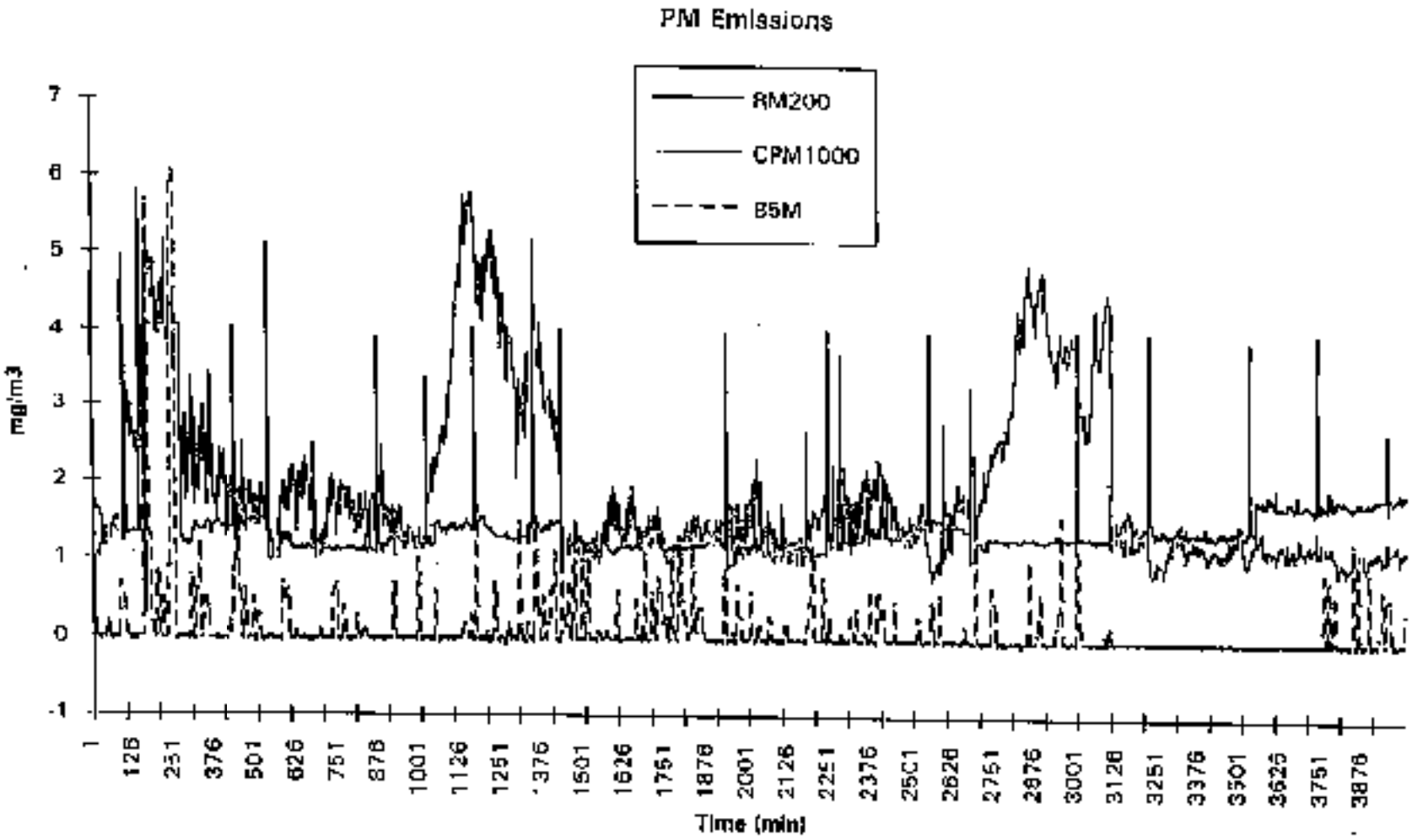

Figure 4-6. Record of CEMs readings for the entire test period.

CHAPTER 5

AVERAGING PERIODS TO COMPLY WITH OPERATING PARAMETER LIMITS

Some operating limits would be complied with on a time averaged basis. Time averaged operating limits are based on ten-minute, one-hour, and/or 12-hour rolling averages. Other limits would be complied with on an "instantaneous" basis. Operating parameter limits based on the shorter averaging periods are more lenient compared with those based on longer averaging periods, thus allowing "stable" operating facilities to potentially emit at higher levels. The shorter averaging period limits put a greater burden on facilities with large swings in operation. The shorter averaging period limits have a practical lower bound due to signal noise and inherent fluctuations typical in any electronics and hardware measurement procedure. Longer averaging periods tend to lead to more restrictive operating limits, but allow for the potential for high emissions over short time periods.

Instantaneous -- For limits to be complied with on an instantaneous basis, measurements would be made continuously and constant without integration (i.e., no averaging period is allowed). At a minimum, individual measurements must be taken every 15 seconds.

10-minute rolling average -- The 10-minute rolling averaging period is considered when the operating parameter can be monitored and controlled on a 10-minute basis (i.e., the response time involved in adjusting the operating parameter is less than 10 minutes); and when either short term excursions may result in unacceptable emissions levels even though long term average emissions may be acceptable, or the operating parameter is indicative of rapid, unrecoverable deterioration of the process effectiveness, thus quick control response is required.

Note that the 10-minute average is almost always used in conjunction with a corresponding one-hour average designed to control average emissions. An exception to this is when the 10-minute average is used to control a equipment manufacturer or designer specification of an air pollution control device. In this case, 10-minute averaging may be used alone.

One-hour rolling average -- The one-hour period is used when there is reduced concern about short term perturbations in emissions levels. This averaging period is currently required for the BIF rule (U.S. EPA, 1992). One-hour averages tend to be more representative of typical operation than 10-minute averages since short excursions are dampened out by longer periods of normal operation, and thus are more suited at controlling average, long term emission levels than 10-minute averages.

12-hour rolling average -- The 12-hour rolling average period is used when there is even less concern about the affect of short-term variations in the parameter on emission levels. It is used solely in situations where feed stream composition measurements are required (where there is an absence of a direct monitor for continuous emissions such as metals).

Rolling average determination -- 10-minute, one-hour, and 12-hour averages used for compliance are calculated every minute on a rolling-average basis. Thus the rolling average levels are updated every minute, irrespective of the averaging period. The one-minute average is determined by the average of the previous four 15-second measurements. This is the same as the approach used in the BIF rule (U.S. EPA, 1992). All 15-second data are used without smoothing, rounding, or data checks.

CHAPTER 6

HOW TO DETERMINE OPERATING PARAMETER LIMITS

6.0 INTRODUCTION

Operating parameter limits are set based on either that demonstrated during comprehensive performance testing or else based on equipment manufacturer and/or designer recommended specifications.

6.1 COMPREHENSIVE PERFORMANCE TESTING

The procedure to determine operating parameter limits which are based on comprehensive performance testing depends on the compliance averaging period. Note that in the below discussions describing the use of comprehensive performance test data to set operating limits, data are to be considered from all runs of a test condition in compliance with the emissions limits, regardless of whether or not the individual runs are in compliance.

Instantaneous limit -- Instantaneous limits are established by determining the average of the parameter over all comprehensive performance test runs at the pertinent test condition. This average becomes the instantaneous limit for that parameter.

10-minute rolling average -- Depending on the application, 10-minute rolling average limits are based on either equipment manufacturer and/or designer specification, or are determined as the average of the highest (or lowest if appropriate) 10-minute rolling averages from each of the comprehensive performance tests.

One-hour rolling average -- Depending on the application, one-hour rolling average limits are determined as either:

- The average of all comprehensive performance test data over all runs at the pertinent test condition. Determined as the average of the sum of all one minute averages occurring

during the testing.

- The average of the highest (or lowest if appropriate) one-hour rolling averages from each of the comprehensive performance test runs at the pertinent test condition.

12-hour rolling average -- 12-hour rolling average limits are determined as the average of the parameter over all of the comprehensive performance test runs at the pertinent test condition.

CHAPTER 7

LIMITS TO CONTROL PCDD/PCDF

7.0 INTRODUCTION

There is currently no monitor for the direct real-time measurement of PCDD/PCDF in stack gas emissions. It will likely be many years before such a device is available due to problems including the large number of PCDD/PCDF congeners as well as isomers within each congener that require monitoring, the fact that PCDD/PCDF are semi-volatile compounds at stack temperatures (present in both the gaseous vapor phase, as well as adsorbed on PM), and the need for extremely low detection limits (on the order of parts per billion). Thus, continuous compliance for PCDD/PCDF is assured indirectly through the monitoring of system operating parameters that are believed to influence PCDD/PCDF formation and control. For municipal waste combustors, monitoring of "Good Combustion Practices" (GCP) is used as a surrogate for assuring continued compliance with PCDD/PCDF emissions (Kilgroe et al., 1990). Many of the GCPs, which can easily be adopted for hazardous waste burners, are discussed below. PCDD/PCDF could be controlled from hazardous waste burners by:

- Limiting PCDD/PCDF formation by:

  -- Maintenance of adequate combustion quality and efficiency to achieve complete burn out of organics and limitation of organic precursors available for PCDD/PCDF formation.

  -- Avoiding formation from low temperature catalytic mechanisms that typically occur in dry particulate matter air pollution control devices. This formation involves surface catalyzed reactions where entrained particulate matter provides the reaction surfaces.

  -- Control of feed constituents that are potential PCDD/PCDF formation precursors, such as PCBs or chlorobenzenes or chlorphenols.

-- Use of formation inhibitors such as sulfur or ammonia, or other proprietary formulations.

Note that in addition, the control of the feedrate of chlorine has been suggested to be potentially related to PCDD/PCDF emissions levels.

· Capturing and/or destroying PCDD/PCDF that have been formed by:

-- Destruction with catalytic oxidizers.

-- Capturing with activated carbon. Activated carbon adsorbs PCDD/PCDF. Carbon can be injected into the flue gas stream and removed in a downstream PM control device. Fixed or fluidized carbon beds can also be used.

-- Capturing condensed phase PCDD/PCDF with a PM control device.

Minimization of the formation of PCDD/PCDF or PCDD/PCDF destruction in hazardous waste burner systems is the preferred control approach compared with PCDD/PCDF capture. PCDD/PCDF capture may only act to transfer it from one emission stream medium to another, and thus the total release of PCDD/PCDF may not be reduced (e.g., removed from flue gas and transferred to solid waste stream).

Specific surrogate combustion device and air pollution control device operating parameters that are recommended for continuous monitoring for assurance of PCDD/PCDF control are summarized in Table 7-1.

7.1 COMBUSTION EFFICIENCY

Maintaining good combustion efficiency and quality involves complete burn out of organics and limitation of the formation of PCDD/PCDF precursors such as chlorinated or non-chlorinated aromatic compounds (e.g., phenol, benzene) as well as aliphatics (Addink and Olie, 1995). A variety of parameters may be considered to be used as indicators of maintaining combustion efficiency. These include flue gas CO and HC content, flue gas flow rate, waste feed rate, exit combustion chamber temperature, monitoring of PICs, primary combustion chamber temperature, combustion chamber oxygen level, waste batch size, feed composition variations, liquid burner settings, and combustion air mixing and distribution.

CO and HC -- Continuous limiting of flue gas CO and HC levels can help ensure good combustion efficiency.

Rationale -- CO and HC flue gas levels are direct indicators of combustion efficiency. Additionally, some studies have suggested that CO may be used as an indirect surrogate for controlling PCDD/PCDF emissions (Kilgroe et al., 1990).

Limit compliance period -- Averaging periods required for compliance are discussed previously in this volume.

Limit basis -- Compliance with MACT standards would be required. The MACT-based levels are discussed in detail in the *Technical Support Document for HWC MACT Standards, Volume III: Selection of Proposed MACT Standards and Technologies*.

Monitoring techniques -- Techniques for continuous monitoring are discussed previously in this volume.

Flue gas flowrate (or production rate) -- A limit on maximum flue gas flowrate would be required.

Rationale-- Flue gas flowrate is a direct measure of the combustion gas velocity through the combustion chamber(s). It is limited to ensure:

- Maximized flue gas residence time to ensure adequate time at temperature for organics destruction and minimize the generation of products of incomplete combustion.

- Minimized back pressure at system joints and seals (e.g., at the junction between a rotary kiln and afterburner).

- Minimized gas flowrate through the air pollution control equipment to ensure that it is not overloaded.

Limit compliance period -- The limit is set as a one-hour rolling average.

Limit basis -- The limit is based on the average of the maximum one-hour rolling averages from each of the comprehensive performance test runs at the pertinent test condition.

Monitoring techniques -- Flue gas flowrate can be monitored with a direct gas flowrate monitor at either the outlet of the last combustion chamber or at the stack. At the outlet of the combustion chamber, there are potential measurement problems due to high temperature, high flue gas acidity, and high particulate loading. At the stack there may be problems due to air infiltration or gas moisture content. Direct measurement techniques include pitot tube, thermal conductivity indicator, sonic flow indicator, rotating disk, or flow constrictor (e.g., baffle plate, venturi, or orifice plate) methods. Flue gas flowrate can also be measured indirectly by combustion air flowrate (not possible for induced draft combustors) or induced draft fan operating power usage (from fan pressure curve measurements). Characteristics of the different measurement techniques are discussed in detail in U.S. EPA (1993) and U.S. EPA (1992).

Surrogate -- Maximum production rate may be used an appropriate surrogate for combustion gas flowrate for industrial furnaces such as light weight aggregate kilns and cement kilns. Depending on the type of system, production rate could be indicated by measurement of parameters such as raw materials feed rate, thermal input, steam production rate (for boilers), or clinker production rate (for cement kilns). The parameter selected must directly correlate with flue gas flowrate.

<u>Waste feed rate</u> -- A limit on the maximum waste feedrate would be required. For industrial kilns, waste feedrate limits are set for each location where waste is fed (e.g., the hot end where the product is discharged, mid-kiln, at the cold end where raw material is fed, at preheater or precalciner). For incinerators, waste feedrate limits are set for each of the different combustion chambers (i.e., different limits for the primary and secondary combustion chambers for controlled air staged incinerators).

Rationale -- A maximum limit is set to avoid overcharging the waste combustion chamber; overcharging may lead to incomplete combustion of feed organics and release of unburned material containing PCDD/PCDF or PCDD/PCDF precursors. For incinerators, waste feedrate limits are established for each combustion chamber to minimize combustion perturbations. For industrial kilns, waste feedrate limits are set for each location where waste is fed (e.g., the hot end, mid-kiln, or the cold end where raw material is fed).

Limit compliance period -- The limit is set as a one-hour rolling average.

Limit basis -- The limit is based on the average of the maximum one-hour rolling averages from each of the comprehensive compliance test runs at the pertinent test condition.

Measurement techniques -- Solid and sludge feedrates can be measured with a variety of techniques including stationary weighing systems (batch scales), conveyor weighing systems (continuous method), volumetric methods (such as auger rotational speeds), level indicators, momentum flowmeters, and nuclear absorption methods. Liquid feedrates can be measured using techniques such as rotameters, orifice meters, flow tube meters, turbine meters, vortex shedding meters, positive displacement meters, and mass flowmeters. Characteristics of the different measurement techniques are discussed in detail in U.S. EPA (1993) and U.S. EPA (1992).

Waste batch size -- Waste batch size is important for batch fed combustion system since it affects the ability of the system to maintain steady-state operations and minimize oxygen deficiencies, puffing, and flame quenching. Thus a limit on maximum waste batch size may be required for batch feeding combustors. This may include batch size limits for hazardous waste burning cement kilns, which feed barrels or pails of wastes at various kiln locations. Batch size limitations are determined by that demonstrated during comprehensive compliance testing. No averaging period is appropriate.

Combustion chamber temperature -- A limit on combustion chamber temperature would be required. Limits are required for each of the chambers of a multi-chamber incinerator; as well as limits for cement kilns at each of the waste feed locations.

Rationale -- High temperature is needed to heat, vaporize, and devolatilize organic waste constituents. Also, generally, the higher the temperature, the greater the level of destruction of organics since the reaction rate for the destruction of organics compounds and the oxidation of their products of incomplete combustion increases with temperature.

Limit compliance period -- Both 10-minute and one-hour rolling average minimum limits are set. A 10-minute rolling averaging period is used to control perturbations in the combustion temperature. A one-hour rolling averaging period is used to control average temperature.

Limit basis -- Both limits are set based on that demonstrated in the comprehensive performance tests. The one-hour rolling average is determined as the average over all runs of the pertinent test condition of the comprehensive performance test.

Measurement techniques -- Combustion gas temperature is usually measured with thermocouples that are shielded from radiation sources. Calibrated optical or infrared pyrometers may be used effectively for measuring temperatures of radiating materials such as flames or burning beds, but are not generally used for measuring gas temperature. It is difficult to reliably measure the combustion zone temperature, especially in some high temperature industrial kilns.

Thus another sampling location within the combustion chamber can be used as an indicator of combustion zone temperature; this location should be as close to the combustion zone as possible. Errors in temperature measurement can be caused by insufficient heat transfer surface, radiation from the flame, or radiation from the incinerator walls.

Control -- Temperature can be controlled by adjusting the waste feedrate, using auxiliary fuel, or by adjusting the feedrate of air or oxygen.

Industrial kilns -- Separate temperature limits are required for each location where hazardous waste is fired (e.g., the hot end where the product is discharged, mid-kiln, at the cold end where raw material is fed, at preheater or precalciner).

Combustion chamber oxygen -- No limit on flue gas oxygen content would be required. An minimum oxygen limit may be beneficiary since maintaining an adequate minimum oxygen level may help to prevent combustion perturbations since oxygen is one of the three necessary ingredients for combustion. However, the other operating parameters discussed in this section are adequate for ensuring high combustion efficiency. Also, both insufficient and excess oxygen levels may lead to increased PCDD/PCDF emissions. Insufficient oxygen results in the formation of PICs which may be PCDD/PCDF precursors; however, insufficient oxygen levels are indicated by high CO and HC flue gas levels, which are required to be continuously monitored. Alternatively, high excess oxygen levels may act to cool the combustion zone, allowing for organics to escape undestroyed. Again, the HC limit should serve as a safeguard against this failure mode. Also, it may not be desirable to operate at high excess oxygen levels since an increase in available oxygen has been shown to increase PCDD/PCDF emissions (e.g., Nottrodt et al., 1990; Manscher et al., 1990; Lenoir et al., 1991). Other reasons for not recommending an oxygen limit include:

- Difficulty in picking one excess oxygen level that is satisfactory for the combustion of different waste types.

- Difficulty in continuously and reliably measuring oxygen concentration at the combustion chamber exit. Measurements are normally made at the stack, where air leakage in between the combustion chamber and the measurement probe location can mask deficiencies in the combustion chamber thus limiting the value of the measurements.

- Several types of combustion chambers are designed to operate at sub-stoichiometric conditions (pyrolytic or gasification systems), where additional oxygen is provided in downstream combustion equipment. For these systems, a minimum oxygen level for the sub-stoichiometric chambers would be inappropriate.

Note that although a minimum oxygen level operating limit is not recommended, stack gas oxygen continuous measurement is required to be able to correct other continuous stack gas measurements (e.g., CO, HC, PM) to a common 7% O_2 standard basis.

Waste and fuel feed composition variations -- Changes in combustor feed composition may adversely affect combustor operational efficiency. For example, a limit on the minimum waste heating value may be appropriate. Spikes and drops in feed compositions may result in regions of cold and/or oxygen deficient gases. However, no limit on waste heating value (or any other feed composition constituent that may effect combustion efficiency) is recommended since other limits discussed above suffice for ensuring adequate combustion control.

Liquid waste burner settings -- In previous guidance, limits on waste burner operating parameters were set to ensure adequate liquid waste atomization and efficient waste/fuel/air mixing. These include atomization fluid pressure, waste heating value, waste viscosity, and burner turndown ratio. However, these are believed to be redundant with the other combustion quality parameters discussed above, and are not recommended. If on a site-specific situation, they are judged to be of importance, it is recommended that limits be set based on manufacturer design and operating specifications.

Air mixing and distribution -- Inadequate mixing between combustion air and waste may lead to oxygen deficient regions and conditions of insufficient residence time at temperature for complete organics burnout. However, monitoring techniques for parameters that are indicative of air/fuel/waste mixing are not available or demonstrated on a full-scale, non-laboratory, scale. Additionally, even if techniques were available, other parameters discussed above are believed to adequately ensure combustion quality.

7.2 LOW TEMPERATURE CATALYTIC FORMATION

PCDD/PCDF may be formed through a low temperature catalytic formation process, typically occurring in the PM control device (e.g., Vogg and Stieglitz, 1986; Kilgroe et al., 1990). Formation from this mechanism has been shown to be due to factors such as PM control device temperature, PM catalytic metals content, and flue gas quench rate.

Dry PM control device temperature -- A limit on maximum PM control device temperature would be required.

Rationale-- PCDD/PCDF has been shown to form in a PM control device that is operated in a typical temperature range from 450 to 750°F (with maximum formation occurring around

570°F). It has been shown that above 400°F and up to about 700°F, PCDD/PCDF emissions can increase by a factor of 10 for every 125°F increase in temperature (U.S. EPA, 1994). A maximum limit on PM control device operating temperature ensures avoidance of operating at temperatures above that demonstrated in the comprehensive performance tests. For cases where there are multiple PM control devices in series, the maximum temperature limit applies only to the first in line, highest temperature device.

Limit compliance period -- Both 10-minute and one-hour rolling average limits are set.

Limit basis -- Both limits are set based on that demonstrated during the comprehensive performance tests. The one-hour limit is set based on the average over all comprehensive performance tests runs.

Measurement techniques -- Flue gas temperature in the PM control device can be measured with similar techniques discussed above for combustion gas temperature.

Feed restriction on metals -- Copper, as well as iron and nickel, have been suggested to aid in catalytic reactions that lead to PCDD/PCDF formation (e.g., Naikwadi and Karasek, 1989; Gullett et al., 1990; Hinton and Lane, 1991). However, the presence of these metals is difficult to control due to their common nature and occurrence. In addition, recent EPA monitored tests on a cement kiln with an ESP have shown that there is no correlation between PCDD/PCDF and copper feedrates (EER, 1995b). For these reasons, an operating limit on maximum feedrate is not required.

Rapid quench -- The flue gas quench rate through the PCDD/PCDF temperature formation region may be important to control the low-temperature catalytic formation of PCDD/PCDF (Fangmark et al, 1994; Gullett et al., 1994). Use of a rapid quench minimizes formation, whereas slow cooling may result in substantial formation; particle gas residence times less than 5 seconds have been shown to be adequate for PCDD/PCDF formation. The above discussed limit on maximum dry PM air pollution control device temperature is sufficient to ensure that flue gas quenching used during the comprehensive performance testing is maintained throughout every-day operation. Additionally, rapid quenching in wet systems does not guarantee controlling PCDD/PCDF, as demonstrated by relatively high PCDD/PCDF levels from wet quench systems (e.g., a couple of hazardous waste incinerators discussed in the *Technical Support Document for HWC MACT Standards, Volume III: Selection of Proposed MACT Standards and Technologies.*

7.3 WASTE CHARACTERISTICS

Waste precursor content -- Certain PCDD/PCDF formation precursors (such as chlorophenols, chlorobenzenes, or chlorinated biphenyls, and other compounds which closely resemble the PCDD/PCDF structure) are believed to be responsible for high PCDD/PCDF stack gas emissions. For example, as discussed in the *Technical Support Document for HWC MACT Standards, Volume III: Selection of Proposed MACT Standards and Technologies*, hazardous waste incinerators that burn chlorobenzene and polychlorinated bi-phenyls have been shown to have high PCDD/PCDF emissions. Thus it may be appropriate to set a limit on the feedrate of suspected PCDD/PCDF precursors. However, other factors such as dry PM control device temperature are believed to be more important to PCDD/PCDF formation. Additionally, the measurement of all suspected PCDD/PCDF precursor compounds may not be feasible. Thus a requirement for the measurement of PCDD/PCDF precursors in combustor feedstreams on a semi-continuous basis is not required. However, the comprehensive performance and confirmatory compliance testing should be conducted using feedstreams that are believed to be fully representative with respect to their content of PCDD/PCDF precursors.

Chlorine feedrate -- Limited bench-scale studies have shown a direct relationship between waste chlorine content (and resulting HCl and Cl_2 flue gas emission levels) and PCDD/PCDF stack gas emissions levels (e.g., Gullett, et al., 1994; De Fre and Rymen, 1989). However, many evaluations on full scale combustion equipment suggest that there is no clear relationship (e.g., Johnke and Stelzner, 1992; Lenoir et al, 1991; Visalli, 1987). Most recently, a comprehensive study conducted for the American Society of Mechanical Engineers statistically analyzed all available PCDD/PCDF emissions and chlorine feed composition data from tests on municipal, medical, and hazardous waste combustors (Rigo et al., 1995). No statistically significant correlation was discovered between the chlorine feed level and PCDD/PCDF emissions. There were a limited number of tests indicating increased PCDD/PCDF emissions with increasing chlorine loading in the waste feed; however, at least an equal number of tests indicated that increased chlorine loading led to a decrease in PCDD/PCDF stack gas emissions. Possible explanations as to why there is no apparent relationship between chlorine feed and PCDD/PCDF levels may include the requirement of extremely low levels of chlorine for PCDD/PCDF formation (demonstrated by the detection of PCDD/PCDF emissions from the combustion of relatively chlorine free diesel and distillate oils) as well as the more dominant influence of other parameters such as PM air pollution control device operation temperature or combustion quality on PCDD/PCDF emissions levels. For this reason, a limit on the maximum chlorine feedrate is not required for compliance with PCDD/PCDF limits. However, note that a maximum feed rate limit for chlorine is required based on limiting of metals volatility and chlorine emissions, as discussed below in more detail, if both total chlorine and LVM and SVM continuous flue gas emissions monitors are not used. Finally, waste with typical average levels of chlorine should

be used during the confirmatory compliance tests.

7.4 FORMATION INHIBITORS

Certain compounds have been demonstrated to inhibit PCDD/PCDF formation. These include sulfur (Gullet et al., 1994; Gullett et al., 1992; Lindbauer et al., 1992; Frankenhaeuser et al., 1993), ammonia (Takacs and Moilanen, 1991), and other proprietary mixtures (Horler and Clements, 1994). The inhibitors may function as both a catalyst poison for the low temperature catalytic formation reaction, and also to eliminate PCDD/PCDF precursors that form prior to the catalytic temperature range. Inhibitor parameters affecting performance include inhibitor feedrate and inhibitor specifications.

Inhibitor injection feedrate -- A limit on the minimum inhibitor injection feedrate would be required. Note that this applies to specific intentionally added inhibitors, and not naturally occurring inhibitors that may be found in typical waste or supplemental fuels (such as sulfur in coal or fuel oil).

Rationale -- Inhibitor performance is expected to improve with increased inhibitor feedrate.

Limit compliance period -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations.

Limit basis -- Both of the limits are set based on comprehensive performance test demonstrations. The one-hour limit is based on the average over all comprehensive performance test runs at the pertinent test condition.

Measurement technique -- Feedrates can be measured with techniques discussed above for waste feedrate.

Inhibitor specifications -- The same type of inhibitor that is used in the comprehensive performance tests must be used in the day-to-day operation. Inhibitor type may be defined by general chemical and physical properties. Inhibitor from a vendor or source that is different from that used in the comprehensive performance testing may be substituted if it can be shown that the inhibitor has similar performance capabilities to that used in the compliance testing. Depending on a site-specific evaluation, this may or may not require demonstration through additional compliance testing.

7.5 AIR POLLUTION CONTROL DEVICES

7.5.1 PM Control Devices

By themselves, PM control devices may have limited PCDD/PCDF control effectiveness. At the extremely low concentrations of concern, PCDD/PCDF is predicted to be in vapor form rather than condensed at PM control device temperatures. However, PM control may be effective for PCDD/PCDF which is adsorbed onto particles containing unburned carbon. Thus all PM control devices discussed below for PM control may also be applicable to PCDD/PCDF control. Note that wet scrubbers may not be effective for PCDD/PCDF vapor control since PCDD/PCDF is not soluble in water. Finally, note that if a continuous monitor for PM is used, then no additional PM control device operating parameter limits are required.

7.5.2 Carbon Injection

Carbon injection may be used for PCDD/PCDF control. Effectiveness is determined by parameters including carbon injection rate, carbon type and specifications, carbon-to-gas mixing, carbon reuse rate, and carbon injection temperature.

Carbon feedrate -- A limit on the minimum carbon injection rate would be required.

Rationale -- In general, increased rates of carbon injection lead to increased levels of PCDD/PCDF control.

Limit compliance period -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations.

Limit basis -- Both of the limits are set based on comprehensive performance test demonstrations. The one-hour limit is based on the average over all comprehensive performance test runs at the pertinent test condition.

Measurement technique -- Carbon feedrate can be monitored with techniques discussed above for waste feedrate monitoring.

Carbon type and specifications -- The same carbon type that was used in the comprehensive performance tests must be used in day-to-day operations. Carbon type may be defined by general chemical and physical properties. Carbon specifications such as chemical properties (e.g., composition, use of additives or enhancers such as iodine or sulfur impregnation)

and physical properties (e.g., particle size, specific surface area, pore size) can significantly affect performance. Carbon from a vendor or source that is different from that used in the comprehensive performance testing may be substituted if it can be shown that the carbon has similar properties to that used in the comprehensive performance testing. Depending on a site-specific evaluation, this may or may not require additional demonstration through performance testing.

Carrier flowrate or nozzle pressure drop -- A limit on minimum carbon injection nozzle pressure drop or carbon carrier flowrate would be recommended.

Rationale-- This is to ensure that the injected carbon particles are properly fluidized in pneumatic transfer lines so that they do not agglomerate prior to injection and to ensure adequate flue gas duct coverage and carbon penetration into the flue gas.

Limit compliance period -- The limit is based on a 10-minute rolling average.

Limit basis -- The limit is set based on equipment manufacturer and/or designer specifications.

Measurement techniques -- Flowrate or pressure drop can be measured using techniques similar to those discussed above for flue gas flowrate.

Carbon recycling rate -- In some cases, all or a portion of the injected carbon that is captured in the PM control device may be reused (i.e., reinjected back into the duct for additional PCDD/PCDF capture if the carbon is not saturated). If carbon recycling is used, a maximum limit on the recycling rate may be appropriate.

Flue gas temperature -- Capture efficiency tends to increase with decreasing flue gas temperature. Thus a maximum flue gas temperature limit may be appropriate. However, the maximum air pollution control device temperature limit requirement for controlling PCDD/PCDF catalytic formation discussed above is sufficient for assuring adequate temperature maintenance at the carbon injection location.

7.4.2 Carbon Bed

Carbon beds may be used for PCDD/PCDF control. Effectiveness is determined by parameters including flue gas flowrate, bed age, and flue gas temperature.

Flue gas flowrate -- To ensure adequate flue gas residence time in the carbon bed, a limit on maximum flue gas flowrate would be appropriate. This limit is already set for other reasons discussed previously.

Carbon type and specifications -- Requirements are identical to those discussed above for carbon injection would also be applicable to carbon beds.

Bed age -- A limit on maximum carbon age (or limit on minimum time between change out of beds) would be recommended.

Rationale -- A limit on bed age is set to ensure that the carbon bed does not become poisoned or saturated, resulting in a reduction of control effectiveness.

Limit basis -- The limit is set initially based on manufacturer specifications. The carbon does not have to be pre-aged for initial comprehensive performance tests). Subsequent confirmatory compliance tests must be conducted within a normal bed changeout schedule. Subsequent comprehensive performance tests must be conducted at the maximum age (i.e., the longest time since the last changeout) of both the most recently changed segment and the least recently changed segment. For example, consider a six segment carbon bed where the segments are operated in series and one segment (the oldest one) is changed out each month. Confirmatory compliance tests can be conducted at any time within this changeout schedule. But comprehensive performance tests must be conducted with the newest segment at least a month old and the oldest segment at least six months old.

Flue gas temperature -- Flue gas temperature in the bed may be important since a temperature spike in the bed may cause adsorbed PCDD/PCDF (and Hg and other heavy metals and organics) to desorb and reenter the stack gas emissions stream. However, because most facilities utilize some type of PM control device upstream of the carbon bed, and inlet temperature to the PM control device must be maintained at a certain level to avoid PCDD/PCDF formation, this is believed to be sufficient to ensure temperature control in the carbon bed.

7.4.3 Catalytic Oxidizer

For catalytic oxidizers, flue gas temperature and flowrate, catalyst age, catalyst type, and flue gas CO, HC and PIC constituent levels may be indicators of catalyst performance.

Flue gas temperature -- Both a limit on minimum and maximum flue gas temperature would be recommended.

Rationale -- Maintaining a minimum inlet temperature is important because catalytic oxidation and destruction rates tends to decrease with decreasing temperature. A maximum limit is important because operation at high temperature can lead to catalyst degradation and reduced catalytic activity.

Limit compliance period -- Minimum limits are based on both 10-minute and one-hour rolling averages. The maximum limit is based on a 10-minute rolling average.

Limit basis -- Minimum limits are determined by the results of the comprehensive performance testing. The one-hour limit is based on the average over all runs of the pertinent test condition. The maximum limit is set based on equipment manufacturer or designer specifications; it is not based on results of comprehensive performance testing.

Measurement techniques -- Flue gas temperature in the catalytic oxidizer control device can be measured with similar techniques discussed above for combustion gas temperature.

<u>Flue gas flowrate</u> -- A limit on the maximum flue gas flowrate through the catalyst would be recommended. This is to ensure that the flue gas has adequate residence time in catalyst bed. This limit has already been addressed previously for other reasons.

<u>Catalyst age</u> -- A limit on the maximum catalyst age would be recommended.

Rationale -- Catalysts can fail due to deactivation from things such as poisoning or over-temperature. This type of failure may not be gradual (e.g., poisoning may occur in a relatively short time period).

Limit compliance period -- Catalyst age is determined by its time in operation.

Limit basis -- Due to the difficulty in determining appropriate age limits through comprehensive performance (or confirmatory compliance) testing, it is recommended that age limits be set with manufacturer and/or designer specifications that are based on expected operating conditions.

<u>Catalyst type</u> -- The same type of catalyst that is used in the comprehensive performance tests must be used in normal operation. Thus, when catalyst is replaced, it must be of the same design and construction material as that used during the comprehensive testing. Design parameters may include loading of catalytic metals, space velocity, and monolith substrate

construction. Minimum catalytic metal loading is important because the catalytic metal level is directly related to catalyst operating performance. Minimum space velocity is important because it is a measure of the gas flow residence time in the catalyst; the longer the time, the more potential for reactions to take place. Catalyst substrate constructions may include monoliths or pellets. Similar catalyst monolith pore density and catalyst washcoat support as that used in the comprehensive performance tests must be used.

Flue gas PICs -- Typically, continuous monitoring of flue gas HC, CO, or speciated PICs are used as a direct indicator of catalyst operating performance. However, due to the low levels typical in incinerator flue gases, and the uncertain relationship between these organic compounds and PCDD/PCDF, this may not be indicative of performance for PCDD/PCDF.

Temperature increase -- Flue gas temperature rise across the catalyst unit may provide an indication of catalyst performance because the oxidation processes generate heat. However, for hazardous waste burner flue gas streams which typically have very low levels of organics, the temperature increase from organic oxidation/destruction may not be measurable or distinguishable from standard variability and measurement noise.

Pressure drop -- Pressure drop across the catalyst bed may be an indicator of proper catalyst to flue gas contacting. Low pressure drop maybe an indication of holes in the bed, thus allowing for gas to pass untreated through the bed. However, this parameter is not recommended since it probably does not have a dominant influence on performance.

TABLE 7-1. PCDD/PCDF ENHANCED MONITORING REQUIREMENTS

Parameter	Compliance With	Limit From	Averaging Period	Limit Determined As
Combustion efficiency				
CO and THC (max)	CO and THC CMS	MACT analysis	1 hour	n/a
Flue gas flowrate (or production rate) (max)	Flowrate or production rate CMS	CPT	1 hour	Avg of maximum 1-hour RAs
Waste feedrate (max)	Feedrate CMS	CPT	1 hour	Avg of maximum 1-hour RAs
Waste batch size (max)	Feedrate	CPT	n/a	Avg over all runs
Combustion chamber temperature (min)	Temperature CMS at each waste feed location	CPT	10 min 1 hour	Avg of minimum 10-min RAs Avg over all runs
Catalytic formation				
Dry PM APCD temperature (max)	Temperature CMS	CPT	10 min 1 hour	Avg of maximum 10-min RAs Avg over all runs
Formation inhibitors				
Inhibitor specifications	Brand/type	CPT	n/a	Same as used in comp test
Inhibitor feedrate (min)	Feedrate CMS	CPT	10 min 1 hour	Avg of minimum 10-min RAs Avg over all runs
Air pollution control techniques				
PM control devices	See Table 3	See Table 3	See Table 3	See Table 3
Carbon injection				
Carbon feedrate (min)	Feedrate CMS	CPT	10 min 1 hour	Avg of minimum 10-min RAs Avg over all runs
Carrier flowrate or nozzle pressure drop (min)	Pressure drop or flowrate CMS	Manufacturer specs	10 min	n/a
Carbon specifications	Brand/type	CPT	n/a	Same as used in CPT
Carbon bed				
Carbon specifications	Brand/type	CPT	n/a	Same as used in CPT
Carbon age (max)	Time in use	CPT	n/a	CPT / manufacturer specs
Flue gas flowrate (or production rate) (max)	Flowrate or production rate CMS	CPT	1 hour	Avg of maximum 1-hour RAs

TABLE 7-1. PCDD/PCDF ENHANCED MONITORING REQUIREMENTS

Parameter	Compliance With	Limit From	Averaging Period	Limit Determined As
Catalytic oxidizer				
Flue gas temperature (min)	Temperature CMS	CPT	10 min 1 hour	Avg of minimum 10-min RAs Avg over all runs
Flue gas temperature (max)	Temperature CMS	Manufacturer specs	10 min	n/a
Catalyst age (max)	Time in use	Manufacturer specs	n/a	n/a

Notes:
CPT : Comprehensive performance tests
CMS : Continuous monitoring system
n/a : Not appropriate
RA : Rolling average

CHAPTER 8

OPERATING PARAMETER LIMITS TO CONTROL PARTICULATE MATTER

8.0 INTRODUCTION

Particulate matter (PM) is a surrogate for semi- and low-volatile metals and semi-volatile organics emissions control since these HAPs are frequently present in PM. PM can be directly monitored on a continuous basis by techniques discussed in previous sections. Alternatively, PM emissions can be controlled through monitoring of waste feed composition, parameters affecting ash partitioning to the combustion chamber ("bottom ash") and flue gas ("fly ash"), and PM air pollution control device operational parameters that are indicative of control device performance. Recommended requirements are summarized in Table 8-1. Note that these would only apply if a continuous PM monitor is not required by the final rule.

8.1 WASTE FEED CONTROL

Waste and fuel ash content, as well as the content of other constituents that may affect PM size distribution generation, may affect PM emissions.

Ash feedrate -- For certain hazardous waste burner system types, a limit on the maximum ash feedrate would be recommended.

Rationale -- A maximum limit is set to prevent overloading of the PM air pollution control device which may lead to increased PM stack gas emissions. Since a fraction of the ash fed to the hazardous waste burner (contained in either the hazardous waste fuels, process raw materials, or auxiliary fuels) is entrained in combustion flue gas, higher ash flue gas loadings may result in increased levels of PM emissions, especially for systems with no PM air pollution control device or systems with ineffective PM control devices (such as some boilers and incinerators). The entrained fraction may be especially high for fluidized bed, rotary kiln, and liquid waste injection type hazardous waste burners. As in the BIF rule, an ash feedrate limit is not required for certain industrial process hazardous waste burners (e.g., cement and aggregate

kilns), where the normal raw materials, which have high ash content, dominate PM ash generation. In these systems, entrained raw materials comprise the majority of PM emissions, and thus a variation in the PM loading to the inlet of a PM air pollution control device is a function of factors other than ash content of hazardous waste fuels. An ash feedrate limit is required for boilers and incinerators.

Limit compliance period -- The limit is based on a 12-hour averaging period. Feedstream sample testing and analysis for ash content frequency must be conducted "as often as necessary to ensure that the results are accurate and up-to-date and to demonstrate that the unit operates within the permit limits" (U.S. EPA, 1992). Feedstream analysis procedures and frequency are developed on a site-specific basis, contained in a "waste analysis plan". Recent guidance on developing hazardous waste incinerator waste analysis plans is contained in U.S. EPA (1994) and U.S. EPA (1995).

Limit basis -- The limit is determined on the average of that demonstrated over all runs from the pertinent comprehensive performance test condition.

Measurement techniques -- Compliance is determined by measurement of ash concentrations in feedstreams and total feedstream feedrates. ASTM Method D482-87 (sample drying and ignition) is recommended for ash analysis of feed materials. Feedrate measurement techniques are discussed above for waste feedrate.

Waste composition -- Certain feedstream inorganic constituents can affect the size distribution of the generated PM (e.g., salts and metal compounds will tend to form fine particulate which is difficult for the PM air pollution control device to control). Limits on maximum metals and chlorine feedrates limits are considered below for other reasons. In site-specific cases, restrictions should be considered on the amounts of other components of waste that are typically burned and believed to affect PM size distribution, as part of the permit conditions. In general, though, there are no specific waste composition limits that are recommended to control PM size distribution.

8.2 ENTRAINMENT

Flue gas flow rate -- A limit on maximum flue gas flowrate through the combustor chamber(s) may act to control of entrainment of PM to flue gas (decreased flowrate may maximize the amount of ash that remains in combustor, and minimize amount of ash that is contained in the combustor flue gases and resulting stack gas PM emissions level). This limit is already recommended for a variety of other reasons discussed above and below.

Sootblowing -- In boilers and other facilities that use heat exchangers for heat recovery, "soot blowing" is used for cleaning of collected PM from heat exchanger tubes (the build-up of PM leads to reduced heat transfer and energy recovery). This can result in temporarily high PM emissions. Typically sootblowing is performed at periodic intervals. As per current BIF regulations (U.S. EPA, 1992), if sootblowing is used, at least one of the comprehensive performance test runs must be conducted during a sootblowing episode.

8.3 AIR POLLUTION CONTROL DEVICES

Operating parameters that are indicative of control device performance are discussed below for the following common PM air pollution control devices: fabric filters, electrostatic precipitators, venturi- and high energy-type scrubbers, ionizing wet scrubbers, and other novel wet scrubbers.

8.3.1 Fabric Filters

The collection efficiency of fabric filters is a function of a variety of factors including:

- Filter type and characteristics (e.g., weave, pore size, thickness).
- Face velocity, which is a function of flue gas flow rate and filter material area.
- Cake build-up, which is dependent on the frequency and level of filter cleaning.
- Particulate matter characteristics, especially size distribution.

Filter failure is typically due to filter holes (tearing and/or rupturing), bleed-through migration of particulates through the filter and cake, and small filter cake "pin-holes". Operating parameters that may provide an indication of fabric filter performance include minimum flue gas flow rate and minimum filter pressure drop. As discussed in more detail below, neither of these operating parameters provides a reliable or adequate measure of fabric filter performance; there is no ideal operating parameter that is truly indicative of fabric filter performance due to fabric filter failure mechanisms. These operating parameters, and this discussion, are also generally applicable to other similar type devices which use a filtering media to capture particulate matter. These may include sintered metal and ceramic filters, and high efficiency particulate air filters.

Flue gas flowrate (or production rate alternative) -- A limit on the maximum flue gas flowrate through the fabric filter would be recommended. An increase in flue gas flow rate results in an increase air-to-cloth ratio (effective filter face velocity) for a fixed filter fabric area,

and a decrease filter PM control efficiency. This limit is already set for a variety of other reasons.

Filter pressure drop -- A limit on the minimum pressure drop across the fabric filter device would be recommended.

Rationale -- Pressure drop may provide an indication of:

- Adequate cake build-up; high pressure drop may indicate sufficient cake build-up and efficient filter performance.

- The presence of filter holes; a decrease in pressure drop may indicate the presence of filter holes and resulting low particulate collection efficiency.

- Leakage between sections of the filter housing and the filters.

However, the pressure change caused by fabric holes may not be measurable, especially in large facilities with multiple chamber filter housing units that operate in parallel. Also, operating at high pressure drop may not be desirable since as mentioned previously, filters fail due to small pinholes which are created from high pressure drop operation, and high pressure drop operation may also be due to undesirable bag blinding or plugging.

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on designer or manufacturer specifications.

Control -- Filter pressure drop can be controlled by adjusting the filter cleaning cycle (maintaining adequate cake build-up) and system maintenance (e.g., change out of old filters, minimization of leakage between selections of the filter and filter housing).

Powder leak detection -- Filter holes may be detected periodically with the use of fluorescent powders. Powder is injected onto the filter; leaks are detected by inspection for the powder on the clean side of the filter using ultra-violet light. The primary limitation of this monitoring technique is that it is a semi-continuous method and thus can not provide a real-time indication of fabric filter performance. This is not recommended as a permit parameter, but may be useful as a facility maintenance practice.

Filter-bag cleaning cycle -- Transient PM emissions spikes are typically directly related to filter-bag cleaning cycles (e.g., with pulse jet, shaking, sonic horns, or other cleaning methods depending on the fabric filter design). Thus it is important to ensure that comprehensive (and

confirmatory) testing include such cycles within the duration of at least one of the tests. To determine actual average emissions levels from test runs with and without cleaning cycles, the BIF guidance soot-blowing averaging procedure should be used when bag cleaning is an occasional event (U.S. EPA, 1992).

8.3.2 Electrostatic Precipitators (ESP)

The PM capture efficiency of ESPs is a function of a variety of parameters including:

- Specific collection area (a function of ESP plate area and flue gas flow rate).
- Particulate matter characteristics such as diameter and resistivity and flue gas viscosity, which are difficult to continuously monitor.
- Electric field collection intensity and particulate matter charge intensity (which are both functions of ESP voltage and current).

Thus, monitoring of flue gas flow rate and power input can be used to assure ESP performance.

Flue gas flowrate (or production rate) -- A limit on maximum flue gas flowrate would be recommended. An increase in flue gas flowrate results in an increase in velocity through the precipitator, a decrease in particle residence time between the charging and collecting plates, and a lower ESP collection efficiency. This limit is already set for a variety of other reasons.

Power input -- A limit on minimum ESP power input would be recommended.

Rationale -- Increased voltage leads to increased electric field strength which results in an increase in the saturation (or limiting) charge level that particulate can obtain, and an increase in charged particulate migration rate to the collection electrode. Increased current leads to an increased particle charging rate, and an increased electric field strength near the collection electrode due to "ionic space charge" contribution and thus increased particle transport rate to the collection electrode. Because for maximum ESP performance, the highest possible values of voltage and current density should be maintained, a limit on minimum ESP power (the product of voltage and current as kVA) is recommended as a continuous performance indicator. Field testing measurements have confirmed that ESP collection efficiency is a relatively strong function of power input (efficiency is a combined function of both voltage and current, and has been shown to be a linear function of power density) (White, 1963). Practical limitations of applied voltage and current include:

- A saturation limit to the maximum amount of charge the particles can take,

- Electrical breakdown of gas throughout the interelectrode space,

- Electrical breakdown of gas in the collected particulate layer (back corona).

Additionally, the power (in particular the current) requirement to an ESP is a function of the inlet flue gas particulate matter loading. The greater the loading, the more current is required; alternately, less current is required at lower loadings. Thus, low power (current) may be an indication of low particulate matter loading. At low particulate loadings it may not be desirable to operate at a high power which was demonstrated during the comprehensive performance tests due to potential operational problems (back corona) and wasted power. For situations where particulate loading varies widely, it may be desirable to maintain a minimum voltage requirement but suspend the minimum current requirement. Note that the applied ESP voltage and current relationship depends of a variety of factors including composition and temperature of gas, and PM mass loading, size distribution, and composition. However, current is directly related (a linear function) to voltage, everything else held constant (McDonald and Dean, 1982).

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average of the minimum one-hour rolling average of each run of the pertinent comprehensive performance test condition.

Collection plate cleaning cycle -- Transient PM emissions levels spikes are typically directly related to collection plate rapping (cleaning) cycles. Thus it is important to ensure that comprehensive (and confirmatory) tests include such cycles within the duration of at least one of the tests. Again, like that discussed above for fabric filters, to determine actual average emissions levels from test runs with and without rapping cleaning cycles, the BIF guidance soot-blowing averaging procedure should be used when rapping is an occasional event (U.S. EPA, 1992).

8.3.3 Venturi- and High-Energy Type Scrubbers

For venturi- and similar type design high energy scrubbers, capture efficiency is maintained by:

- Providing high relative velocity between solid PM and liquid droplet phases to enhance particle/droplet collisions.

- Minimizing the diameter of the atomized liquid scrubber droplets.

- Minimizing entrainment of agglomerated PM/liquid droplets.

Thus, scrubber pressure drop, blowdown rate (or liquid turbidity), liquid-to-gas ratio, liquid injection nozzle pressure, and liquid surface tension may provide an indication of scrubber performance.

Pressure drop -- A limit on minimum pressure drop would be recommended.

Rationale -- Venturi scrubber removal efficiency is a strong function of pressure drop (and particulate diameter) (EPA, 1989). Particle capture in venturi scrubbers is a function of the degree of liquid atomization that is achieved and of the amount of mixing and relative velocities between the flue gas particulate and liquid droplets, which are both functions of the flue gas velocity across the device (pressure drop across the venturi is a direct measure of flue gas velocity).

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average of the minimum one-hour rolling average of each run of the pertinent comprehensive performance test condition.

Control -- Pressure drop is most commonly controlled through the adjustment of the throat area. The pressure drop is typically measured across the entire scrubber, including the demister.

Liquid blowdown rate (or liquid turbidity) -- A limit on minimum liquid blowdown rate or maximum liquid turbidity would be recommended.

Rationale-- This is to control the dissolved and suspended solids content ("turbidity") in the liquid and is important because increased solids content of the scrubber liquid increases the amount of particulate solids that can be reentrained in the scrubber exit gas. Additionally, high liquid turbidity may act to plug system components leading to a deterioration in system performance. Compliance can be demonstrated by direct monitoring of the scrubber liquid turbidity or by indirectly maintaining a prescribed liquid blowdown rate. Liquid blowdown is the fraction of the liquid captured and removed from the scrubber that is not recycled for reuse back into the scrubber. Greater blowdown means that less recycled liquid is mixed with fresh liquid, and that the liquid in the scrubber is cleaner. However, more liquid is wasted. A liquor "conditioning" period may be needed prior to testing to establish an equilibrium scrubber liquor composition.

Compliance period and basis -- Both 10-minute and one-hour minimum (or maximum) rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average of the minimum (or maximum) one-hour rolling average of each run of the pertinent comprehensive compliance test condition.

Measurement techniques -- Liquid turbidity can be measured with a density transmitter instrument; liquid blowdown rate can be monitored with a variety of liquid flowrate devices discussed elsewhere.

Liquid-to-gas ratio -- A minimum liquid-to-gas ratio limit would be recommended.

Rationale -- At low liquid-to-gas ratios, capture efficiency decreases due to an insufficient number of liquid droplet targets. Liquid-to-gas ratio is maintained by adjusting the liquid injection rate or flue gas flowrate. Note that at very high liquid-to-gas ratios, efficiency may also decrease due to a change in the droplet size distribution formed in the scrubber; however, due to the lower probability of this occurring and lesser effect on capture efficiency, a limit on maximum liquid-to-gas ratio is not recommended.

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average of the minimum one-hour rolling average of each run from the pertinent comprehensive performance test condition. Note that for this and other "normalized" parameters which are not measured directly by one measurement technique, for facilities where one of the parameters does not change much (e.g., cement kiln flue gas flowrate), it may make more sense to limit only the parameter that changes, and not the ratio.

Measurement techniques -- Liquid-to-gas ratio is determined by measurement of liquid injection rate and flue gas flowrate. Measurement techniques for both of these parameters have been discussed above.

Liquid injection nozzle pressure -- If nozzles are used to atomize the scrubbing liquid, a limit would be set on minimum nozzle pressure to ensure adequate liquid atomization. The limit is set based on manufacturer specifications. Compliance is based on a 10-minute rolling average time period.

Liquid surface tension -- Scrubber liquid surface tension affects scrubber performance. Decreasing liquid surface tension leads to improved scrubber emissions performance. With high liquid surface tension, particles tend to "bounce" off the liquid droplets and are not captured; high

surface tension also has an adverse effect on droplet formation. However, since surface tension is not believed to be a dominant parameter for scrubber performance, and there is no easy way to continuously monitor it, it is not recommended.

8.3.4 Ionizing Wet Scrubbers

Ionizing wet scrubbers are a combination of wet ESPs and packed bed wet scrubber technologies. Thus they have similar operating parameter requirements to those discussed above for wet scrubbers and ESPs for PM control.

8.3.5 Other Wet Scrubber Types

In addition to venturi and ionizing types discussed above, there are many other different types of wet scrubbers that can be used for particulate matter control such as collision, condensing free-jet, and froth types. These scrubbers may have similar type of operating parameters to those discussed above. However, some may have other monitoring requirements such as minimum steam/air flow rate or injection pressure for condensing free jet types.

8.4 INDIRECT PM EMISSIONS MONITORS

Indirect continuous PM emissions monitors such as opacity or triboelectric monitors may be an effective tool for detecting PM spikes and deviations from normal operation (such as those created from fabric filter pin holes and bleed-through). The use of these techniques is a preferred alternative in conjunction with air pollution control device operating parameter limits discussed above if a continuous emission monitoring technique is not used. However, these techniques are not sufficient by themselves to be used as a compliance technique with PM emissions standards.

TABLE 8-1. PARTICULATE MATTER ENHANCED MONITORING REQUIREMENTS

Parameter	Compliance With	Limit From	Averaging Period	Limit Determined As
Feed Control				
Ash Feed rate (max)	Feedrate CMS and ash analysis	CPT	12 hours	Avg over all runs
Entertainment control				
Flue gas flowrate (or production rate) (max)	Flowrate or production rate CMS	CPT	1 hour	Avg of maximum 1-hour RAs
Air pollution control devices				
Fabric filter				
Filter pressure drip (min)	Pressure drop CMS	Manufacturer specs	10min 1 hour	n/a
Flue gas flowrate (or production rate) (max)	Flowrate or production rate CMS	CPT	1 hour	Avg of maximum 1-hour RAs
Electrostatic precipitator				
Power input (kVA) (min)	Voltage and current CMS	CPT	10 min 1hour	Avg of minimum 10-min RAs Avg over all runs
Flue gas flowrate (or production rate) (max)	Flowrate or production rate CMS	CPT	1 hour	Avg of maximum 1-hour RAs
Wet scrubbers				
Pressure drops (min)	Pressure drop CMS	CPT	10 min 1hour	Avg of minimum 10-min RAs Avg over all runs
Liquid feed pressure (min)	Pressure CMS	Manufacturer specs	10 min	n/a
Liquid blowdown rate (min) or turbidity (max)	Liquid flowrate or turbidity CMS	CPT	10 min 1hour	Avg of min (max) 10-min RAs Avg over all runs
Liquid/gas ration (min)	Liquid and gas flowrate CMS	CPT	10 min 1hour	Avg of minimum 10-min RAs Avg over all runs
Ionizing wet scrubber	Same as ESP and wet scrubbers	Same as ESP and wet scrubbers	Same as ESP and wet scrubbers	Same as ESP and wet scrubbers

Notes:

CPT: Comprehensive performance tests

CMS: Continuous monitoring system

n/a: Not appropriate

RA: Run average

CHAPTER 9

OPERATING PARAMETER LIMITS TO CONTROL MERCURY

9.0 INTRODUCTION

As discussed above, mercury continuous emissions monitoring (with either total species or elemental mercury devices) may be used. If not, operating parameters including mercury feedrate, chlorine feedrate, combustion temperature, and mercury air pollution control device operating parameters may be appropriate for continuous assurance for controlling mercury stack gas emissions levels. Operating parameters that are recommended for mercury control are summarized in Table 9-1.

9.1 COMBUSTOR OPERATING PARAMETERS

Mercury feedrate -- A limit on maximum mercury feedrate would be recommended.

Rationale -- The amount of mercury fed to the combustor directly affects mercury flue gas emissions and the ability of control equipment to remove mercury. Typically emission rates increase with increasing feedrates. A limit is set on maximum total feedrate (in all streams including hazardous waste, raw materials, and fossil fuels). Unlike other metals, no limit is set on maximum total metals feedrate in pumpable hazardous wastes since mercury is highly volatile in any form.

Limit compliance period and basis -- The mercury feedrate limit is set on a 12-hour rolling average basis. The limit is based on the average of all runs of the pertinent comprehensive performance test condition. Mercury feedstream analysis requirements are similar to those discussed above for PM ash feedrate control.

Measurement techniques -- Levels are monitored by measuring metals concentrations in individual feedstreams and individual feedstream feedrates. Mercury analysis (digestion and analytical techniques) is recommended with SW-846 7470 or 7471 (cold vapor atomic absorption spectroscopy). Feedstream measurements techniques are similar those discussed above for ash feedrate.

Chlorine feedrate -- Chlorine feedrate may be important when wet scrubbers are used for mercury control since wet scrubbers are effective at controlling soluble mercury salts, but not effective at controlled unchlorinated mercury species. Thus a limit on minimum chlorine feedrate may be appropriate in this case. However, since only very small amounts of chlorine are required for the typically low levels of mercury, a minimum limit on chlorine is not recommended.

Combustion chamber temperature -- At typical mercury feedrates and combustion temperatures, all mercury vaporizes in the combustion chamber and remains in the vapor phase through the entire system (including the lower temperature air pollution control equipment). Thus, a maximum limit is not recommended for the control of mercury emissions. A limit on maximum combustion chamber temperature would only be appropriate in cases of extremely high mercury feedrate and relatively low combustion chamber temperature, where it is possible that the equilibrium vapor pressures of the mercury may be exceeded.

9.2 AIR POLLUTION CONTROL DEVICES

9.2.1 Wet Scrubbers

As discussed above, wet scrubbers may be effective at controlling certain water soluble forms of mercury, primarily mercury chloride (HgCl). Operating parameters that are indicative of mercury control are similar to those discussed for PM and chlorine control. Note that if a "total species" mercury continuous emissions monitor is used, then no monitoring of operating parameters related to mercury is required. However, if only an elemental mercury (Hg°) continuous emissions monitor is utilized, wet scrubber operating parameters are to be monitored since the mercury salt emissions are not accounted for by an elemental mercury monitor.

9.2.2 Carbon Injection

Carbon injection can be used for controlling mercury emissions. Operating parameters that are indicative of mercury control are identical to those as discussed above for PCDD/PCDF control.

9.2.3 Carbon Beds

Carbon beds can be used for controlling mercury emissions. Operating parameters that are indicative of mercury control are identical to those as discussed above for PCDD/PCDF control.

9.2.4 Others

Other techniques that may be used for mercury control include selenium filters and sodium sulfide injection, both of which are discussed in some detail in *Technical Resource Document for HWC MACT Standards, Volume I: Description of Source Categories*. Sodium sulfide injection monitoring parameters may be analogous to those for carbon injection. Selenium filter parameters may be analogous to those for carbon beds and fabric filters.

TABLE 9-1. MERCURY ENHANCED MONITORING REQUIREMENTS

Parameter	Compliance With	Limit From	Averaging Period	Limit Determined As
Feedcontrol				
Mercury feedrate (max)	Feedratre CMS and mercury analysis	CPT	12 hours	Avg over all runs
Air Pollution Control Devices				
Carbon injection	See Table 7-1	See Table 7-1	See Table 7-1	See Table 7-1
Carbon bed	See Table 7-1	See Table 7-1	See Table 7-1	See Table 7-1
Wet scrubbers	See Table 7-11	See Table 7-11	See Table 7-11	See Table 7-11

Notes:
CPT: Comprehensive performance tests
CMS: Continuous monitoring system
n/a: Not appropriate
RA: Rolling average

CHAPTER 10

OPERATING PARAMETER LIMITS TO CONTROL SEMI-VOLATILE AND LOW-VOLATILE METALS

10.0 INTRODUCTION

Semi-volatile (SVM) metals include lead and cadmium. Low-volatile (LVM) metals include arsenic, barium, beryllium, and chromium. As discussed in previous sections, although direct continuous flue gas emissions monitors for SVM and LVM metals are being developed, they are not currently demonstrated and may not be commercially available for some time. Thus, without direct emission monitors, surrogate operating parameters that are indicative of metals behavior in hazardous waste burners are used. These potentially include:

- Combustor operating parameters:
  - Metals feedrate
  - Metals volatility, which is primarily a function of:
    - Chlorine feedrate
    - Combustor temperature
- Air pollution control device operations

Operating parameters that are recommended for LVM and SVM control are summarized in Table 10-1.

10.1 COMBUSTOR OPERATING PARAMETERS

Metals feedrate -- A limit on maximum metals feedrate would be recommended.

Rationale -- The quantity of metal fed to the combustor may affect emissions. Typically, metals emission rates increase with increasing metals feedrates. For LVM, limits are set on:

- Maximum total feedrate (in all streams including hazardous waste, raw materials, and fossil fuels)

- Maximum total metals feedrate in pumpable hazardous wastes.

Different limits are set for LVM in pumpable feedstreams since they may partition at a higher rate to the combustion flue gas (and thus be emitted at a higher rate) than metals in non-pumpable feed streams. Like discussed above for Hg, for SVM, limits are only set on maximum total feedrate, because partitioning between the combustion gas and bottom ash or product does not appear to be affected by the physical state of the feedstream (for typical SVM levels and combustion chamber temperatures, all SVM is predicted to vaporize to the combustion gas).

Limit compliance period and basis -- The SVM and LVM feedrate limits are set on a 12-hour rolling average basis. The limits are based on the average of all runs from the pertinent comprehensive performance test condition. LVM and SVM feedstream analysis requirements are similar to those discussed above for PM ash feedrate control.

Measurement techniques -- Feedrate levels are determined by measurements of metals concentrations in individual feed streams and individual feed stream feedrates. Metals analysis methods (digestion and analytical techniques) are outlined SW-846 (U.S. EPA, 1992). Metals analytical techniques are summarized in Table 10-2. The appropriate sample digestion technique (SW-846 Series 3000 Method) is chosen depending on the feedstream phase and analytical method to be used. Feedstream feedrate (solid and liquid) measurement techniques have been discussed above in previous sections.

Metals spiking -- The grouping of metals by expected volatility behavior (and resulting partitioning in the combustor system) allows for the use of only one metal within each grouping to be used as a surrogate for other metals in the volatility grouping during performance testing, i.e., spiking of combustor feedstreams is only required for one metal in each of the volatility groupings to demonstrate compliance.

Chlorine feedrate -- An operating limit on maximum chlorine feedrate to the combustion system would be recommended. The limit is based on the total chlorine content in all feedstreams; this includes organic and inorganic chlorine sources.

Rationale-- Chlorine levels may affect metals emissions since chlorinated metal species are more volatile than unchlorinated metals and are thus more difficult to control (Barton et al., 1990).

Limit compliance period and basis -- The chlorine feedrate limit is set on a 12-hour rolling average basis. The limit is based on the average of all runs from the pertinent comprehensive performance test condition. Chlorine feedstream analysis requirements are similar to those discussed above for PM ash feedrate control.

Measurement techniques -- The total chlorine feedrate is determined by individual measurements of chlorine concentration in feed streams and feed stream feedrates. SW-846 Method 5050 (or ASTM D808) for sample preparation and SW-846 Methods 9250, 9251, 9252, or 9253 for analytical are recommended for chlorine sample analysis. An option for aqueous wastes is to analyze for total organic halogens with SW-846 Methods 9020 or 9022 and inorganic chloride according to the methods discussed above.

Combustion chamber temperature -- For the BIF rule, an operating limit is set on maximum combustion chamber temperature (U.S. EPA, 1992). This was done to ensure operation at temperatures that do not lead to volatilized metals emissions. Increasing combustion chamber temperature leads to increased metals volatility, which may result in an increase in metals stack gas emissions. As previously discussed, highly volatile metals remain as vapor and may pass uncaptured directly through most air pollution control systems. Lower volatility metals (including LVM and SVM) which vaporize in the combustion chamber tend to condense at lower air pollution control system temperatures either into or onto particles in the sub-micron size range, which is the most difficult to remove in air pollution control system. However, further evaluation suggests that although a maximum limit on combustion chamber temperature may make sense for the control of metals emissions based on theoretical considerations and limited laboratory or pilot scale research, in practice it is not considered as necessary for reasons, discussed in more detail below, including:

- Most metals are typically either highly volatile or highly non-volatile at common combustion temperatures (supported by both theoretical and experimental test evidence); thus small changes in temperature (as would typically be expected in combustion units) do not impact metals volatility (and resulting stack gas emissions levels).

- Combustion chamber temperature is difficult to measure, especially for industrial kilns.

- Analyses of BIF trial burn data does not provide any support for a relationship between combustion chamber temperature and stack gas metals emissions levels (for more details, see *Technical Support Document, Volume VI: Miscellaneous Technical Issues*).

For SVM, in most cases, typical combustion chamber temperatures are high enough so that all of the metals volatilize in the combustion chamber. Thus, increases in temperature beyond typical combustion chamber operating levels will not impact the SVM load to the air pollution control system (and resulting stack gas emissions levels). This is supported by analyses of the BIF trial burn data showing that SVM partitions mostly to the captured particulate matter and dust in the air pollution control system (in general, all SVM vaporizes in the combustion chamber and condenses at the lower operating temperatures of the air pollution control system) (EER, 1994). This behavior is also supported by theoretical modeling (Clark and Rizeq, 1991).

LVM would not be expected to vaporize entirely in the combustion chamber; thus there may be a chance that operating at higher than demonstrated combustion chamber temperature may result in additional metals vaporization and an increase in load (and emissions) to the air pollution control system (as mentioned above, vaporized metals condense on small particles which are difficult to capture in the air pollution control system). However, this may not be important since the amount of vaporization at typical combustion temperatures, and the amount of additional vaporization at higher than typical temperatures, may be negligible compared to the amount of LVM contained in non-volatilized entrained flue gas particulate matter, which is present at particularly high levels in cement kilns, aggregate kilns, fluidized and rotary kiln incinerators, and pulverized coal boilers.

Analyses of BIF trial burn data has not indicated any relationship between combustion chamber temperature and LVM (or SVM or mercury) stack gas emissions. Note that this may be due to the difficulty in observing trends from data taken from a number of facilities; there is a considerable amount of variance from one facility to another due to differences in control devices, feed rates, operating parameters, and measurement techniques. These effects of facility specific differences may obscure trends due to a single parameter. In particular, combustion chamber temperature is very difficult to accurately measure, especially from cement and light weight aggregate kilns. Temperature measurements are taken at different locations with different instruments, making it difficult to compare results from different facilities. In any case, the fact that there was no apparent relationship between combustion chamber temperature and metals stack gas emissions (LVM as well as SVM or mercury) may be interpreted to imply that other parameters besides combustion chamber temperature are more dominant in influencing stack gas

emissions levels.

Another reason against setting a maximum temperature limit is, as mentioned, that it is very difficult to accurately measure combustion chamber temperature (Clark and Rizeq, 1991). Optical techniques offer the only practical way to directly measure combustion chamber temperature in an industrial kiln. However, since the "hot spot" in a kiln moves due to changes in kiln shape length and shape, misaligned optical devices may record an apparent temperature which is below the actual temperature. Thermocouples can be used to measure temperature at the cold end of industrial kilns. However, there is no guarantee that the downstream temperature is a good indicator of the combustion chamber temperature due to the cyclic, non-steady state operation of industrial kilns.

Additionally, the requirement of a maximum temperature limit is in conflict with demonstration of operation at a minimum temperature limit for adequate organics destruction. Thus the addition of a maximum combustion chamber temperature limit would increase the testing condition requirements (and thus costs and complexity) of the comprehensive compliance testing program.

Note that under strictly theoretical considerations, it has been shown that for particular cases, higher combustion chamber temperatures should lead to increased metals emissions (for instance, certain SVM at very high feedrates where complete vapor saturation is predicted to occur) (Clark and Rizeq, 1991).

10.2 AIR POLLUTION CONTROL DEVICES

PM air pollution control device type and associated control parameters discussed above are also equally applicable to SVM and LVM control. Additionally, the operating temperature of the air pollution control device or system may be of particular important to SVM control. Specialized sorbent specifically designed for metals control may also be used.

Operating temperature of air pollution control device -- It may be expected that for metals which volatilize in the combustion chamber and are carried out with the flue gas, the temperature of the particulate matter control device will influence the subsequent degree of condensation and control (i.e., lower temperature resulting in a higher degree of condensation and control). Thus, a maximum temperature limit may help to ensure that these types of metals emissions are being adequately controlled. However, there was no apparent correlation on metals emissions from analyses of BIF trial burn data. Additionally, a maximum control device temperature limit is already being recommended to control PCDD/PCDF formation.

Metal capturing sorbents -- Sorbents such as kaolin, bauxite, silica, alumina, and clays, are currently being developed to control semi-volatile metals emissions (e.g., Wu et al., 1995). No hazardous waste burning facilities are currently intentionally using these control techniques, however they may in the future. The sorbents can be added directly to the feed, or injected separately downstream of the combustor. Operating parameter requirements may be analogous to carbon injection and dry scrubbing technologies discussed in other sections. Note that in site-specific cases where waste and other feedstream materials may potentially contain these types of metal capturing ingredients, monitoring of waste composition during the comprehensive performance testing (and during regular operation) may be appropriate.

TABLE 10-1. LVM AND SVM ENHANCED MONITORING REQUIREMENTS

Parameter	Complince With	Limit From	Averaging Period	Limit Determined As
Feedcontrol				
Metals feedrarte (max)				
Total feedstreams	Feedrate CMS and metal analysis	CPT	12 hours	Avg over all runs
Pumpable feedstreams	Feedrate CMS and metal analysis	CPT	12 hours	Avg over all runs
Chlorine feedrate (max)	Feedrate CMS and chlorine analysis	CPT	12 hours	Avg over all runs
PM air pollution control devices	See Table 8-1	See Table 8-1	See Table 8-1	See Table 8-1

Notes:
CPT: Comprehensive performace tests
CMS: Continuous monitoring system
n/a: Not appropriate
RA: Rolling average

TABLE 10-2. ANALYTICAL METHODS FOR METALS IN FEEDSTREAMS

Metal	SW-846 Analytical Method
Low Volatile Metals	
Antimony	6020, 7040
Arsenic	6020, 7060, 7061
Barium	6010, 6020, 7080
Beryllium	6010, 6020, 7090, 7091
Chromium (total)	6010, 6020, 7090, 7091
Semi Volatile Metals	
Cadmium	6010, 6020, 7130, 7131
Lead	6010, 6020, 7420, 7421
High Volatile Metals	
Mercury	7470, 7471

6010 method: atomic emission spectroscopy (inductively coupled plasma)
6020 method: mass spectrometry
7000 series methods: atomic absorption spectroscopy (furnace, flame, hydride, cold vapor)

CHAPTER 11

OPERATING PARAMETER LIMITS TO CONTROL CHLORINE

11.0 INTRODUCTION

As discussed above, the use of continuous emissions monitors for both hydrogen chloride (HCl) and chlorine gas (Cl_2) (or possibly HCl alone in certain cases) may be used as a direct indicator of total chlorine emissions. However, if a chlorine continuous emissions monitor is not used then system operating parameters influencing chlorine emissions levels are monitored to ensure continuous compliance, including:

- Combustor operating parameters including feedstream chlorine and caustic feedrates.

- Chlorine air pollution control device (e.g., dry and wet scrubbers) operating parameters.

Operating parameters that are recommended for chlorine control are summarized in Table 11-1.

11.1 COMBUSTOR OPERATING PARAMETERS

Chlorine feedrate -- Typically, chlorine emissions rates increase with increasing chlorine feedrate. Thus a limit on the maximum feedrate of chlorine would be recommended based on the total chlorine contained in all feedstreams. This includes both organic and inorganic chlorine sources. Feedrate is determined by analysis of chlorine concentrations in individual feedstreams and feedstream feedrate measurements. Measurement methods, limit averaging periods, and bases to set limits on are discussed previously in LVM and SVM section.

Caustic feedrate -- Certain feed constituents may act to control chlorine flue gas emissions (e.g., feed content of calcium or sodium or potassium). Thus a limit on the minimum feedrate of these chlorine controlling parameters may be appropriate. However, this limit is not recommended in general since in practice chlorine control is primarily based on chlorine feedrate control and the use of an air pollution control device. In site-specific cases where feed

composition is believed to significantly influence chlorine control this limit may be appropriate.

11.2 AIR POLLUTION CONTROL DEVICES

11.2.1 Dry and Spray Dryer Scrubbers

Dry and spray-dryer scrubbing performance is impacted primarily by caustic feedrate, parameters influencing caustic-to-gas mixing, caustic type and specifications, and temperature at location of injection.

Caustic feed rate -- A limit on minimum caustic injection rate would be recommended.

Rationale -- In general, increased levels of caustic injection lead to increased levels of acid gas control. Ideally compliance should be based on maintaining a minimum ratio of the caustic to that of the flue gas acid content; however this is not possible without either detailed and accurate waste knowledge or a continuous HCl monitor.

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average over all runs of the pertinent comprehensive performance test condition.

Measurement techniques -- Feedrate measurement techniques have been discussed above.

Caustic type and specifications -- The same caustic type that was used in the compliance tests must be used in everyday operations. Caustic type may be defined by general chemical and physical properties. Caustic specifications such as chemical properties (e.g., composition, use of additives or enhancers) and physical properties (e.g., particle size, specific surface area, pore size) can significantly affect performance. Caustic from a vendor or source that is different from that used in the compliance testing may be substituted if it can be shown that the caustic has similar properties to that used in the compliance testing. Depending on site-specific situations, this may or may not require additional demonstration through compliance testing.

Carrier flowrate or nozzle pressure drop -- A limit on minimum caustic injection nozzle pressure drop or caustic carrier flowrate would be recommended.

Rationale -- This is to ensure that caustic particles are properly fluidized in pneumatic transfer lines so that they do not agglomerate prior to injection. Also, this is to ensure adequate caustic flue gas duct coverage (caustic penetration into the flue gas).

Limit compliance period and basis -- The limit is set based on manufacturer specifications. An instantaneous limit is set. No averaging is used.

Measurement techniques -- Measurement techniques for flowrate and pressure drop have been discussed above.

Caustic injection temperature -- Capture efficiency is a function of temperature; in general, capture efficiency tends to increase with decreasing temperature. However, a limit on maximum air pollution control device temperature already set for other reasons is sufficient to ensure this parameter is within an adequate range.

Caustic recycling rate -- Captured used caustic in a particulate matter control device may be recycled for additional use. If recycling is used, it may be appropriate to set a limit on the maximum recycling rate, similar to that discussed above for carbon injection.

11.2.2 Wet Scrubbers

There are many different types of wet scrubbers that are used for chlorine control. These include spray towers, packed beds, plate tray, froth, and venturi and ionizing wet scrubbers, some of which were discussed above for PM control. For acid gas control, general wet scrubber parameters including scrubber liquid pH, liquid-to-gas ratio, and scrubber pressure drop may be indicative of assuring control device performance.

Liquid pH -- A limit on the minimum pH of the effluent scrubber liquid would be recommended.

Rationale -- At lower pH levels (more acidic), scrubbing liquids have decreased acid gas solubility (especially for Cl_2). Additionally, the pH should be maintained to assure that the scrubbing liquid has adequate capacity to remove acid gases (i.e., the pH of the solution exiting the scrubber should be limited to assure that the scrubber is not being overloaded with acid). Effluent liquid pH level information can also be used for effective handling of the waste liquid. The pH is controlled by addition of caustic materials to the liquid prior to introduction into the scrubber unit or by increasing liquid blowdown (with a corresponding increase in liquid fresh makeup water).

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average of the minimum one-hour rolling average of each run of the pertinent comprehensive performance test condition.

Measurement techniques -- The pH is monitored with a continuous liquid pH meter.

Liquid-to-gas ratio -- A limit on minimum liquid-to-gas ratio would be recommended.

Rationale -- A limit on liquid-to-gas ratio is set is to ensure proper wetting of scrubber internal packings or trays and/or to facilitate sufficient liquid and gas contacting. Liquid-to-gas ratio is maintained by adjusting the liquid injection rate and/or flue gas flow rate.

Limit compliance period and basis -- Both 10-minute and one-hour minimum rolling averages are set based on comprehensive performance test demonstrations. The one-hour limit is set based on the average of the minimum one-hour rolling average of each run of the pertinent comprehensive performance test condition.

Measurement techniques -- Liquid-to-gas ratio is monitored by measurement of both flue gas flow rate and liquid injection rate. These techniques have been discussed above.

Pressure drop -- Pressure drop across plate tray- and venturi-type scrubbers may be important in assuring performance. Increasing pressure drop typically corresponds to increasing control performance as discussed above in the wet scrubber PM control section. However, pressure drop across acid gas controlling packed bed and spray towers is not that important. Thus, except in site specific cases, a limit on minimum wet scrubber pressure drop is not recommended. Monitoring methods and averaging times are discussed in more detail above on the section addressing PM control.

TABLE 11-1. TOTAL CHLORINE ENHANCED MONITORING REQUIREMENTS

Parameter	Compliance With	Limit From	Averaging Period	Limit Determined As
Feedcontrol				
Chlorine feedrate (max)	Feedrate CMS and chlorine analysis	Comp test	12 hours	Avg over all runs
Air Polluation Control Devices				
Wet Scrubbers				
Pressure drop (min)	Pressure drops CMS	CPT	10 min 1 hour	Avg of minimum 10 min RAs Avg over all runs
Liquid feed pressure (min)	Pressure CMS	Manufacturer specs	10 min	n/a
Liquid pH (min)	pH CMS	CPT	10 min 1 hour	Avg of minimum 10 min RAs Avg over all runs
Liquid/gas ratio (min)	Liquid and gas flowrate CMS	CPT	10 min 1 hour	Avg of minimum 10 min RAs Avg over all runs
Dry and semi-dry scrubbers				
Caustic feedrate (min)	Feedrate CMS	CPT	10 min 1 hour	Avg of minimum 10 min RAs Avg over all runs
Carrier flowrate or nozzle pressure drop (min	Pressure drop or flowrate CMS	Manufacturer specs	10 min	n/a
Caustic specifications	Brand/type	CPT	n/a	Same as used in CPT

Notes:
CPT: Comprhensive performance tests
CMS: Continuous monitoring system
n/a: Not appropriate
RA: Rolling average

CHAPTER 12

OPERATING PARAMETER LIMITS TO CONTROL FUGITIVES

Fugitive emissions can result from leaks from the combustion chamber(s), air pollution control equipment, or any ducting that connects them. To control fugitive emissions one of the following must be demonstrated:

- Keep the system totally sealed; for example, for forced draft systems (e.g., positive pressure incinerators such as liquid injection units), a limit on combustion chamber pressure is set.

- Maintain the system at pressure lower than atmospheric. For example, induced draft (negative pressure) incinerations, such as rotary kilns, must remain below atmospheric to avoid fugitive emissions through rotary seals or other system leaking points.

- Use some other means of control demonstrated to provide fugitive emissions control that is equivalent to maintenance of negative gauge system pressure.

In the cases where a system pressure limit would be set, compliance is required on an instantaneous basis. The limit is set based on manufacturer of designer specifications. Combustor system pressure is measured typically with piezoelectric electron pressure transducers.

Note that in site specific situations, such as munitions incinerators, fugitive emissions may be a problem even when negative gauge pressure is maintained. Such cases may require continual video surveillance of the kiln to ensure there are no leaks.

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APPENDIX A

PERFORMANCE SPECIFICATION FOR PM CEMS

PERFORMANCE SPECIFICATION 11 -- Specifications and test procedures for particulate matter continuous monitoring systems in stationary sources

1. *Applicability and Principle*

1.1 Applicability. This specification is to be used for evaluating the acceptability of particulate matter continuous emission monitoring systems (CEMS) at the time of or soon after installation and whenever specified in the regulations. The CEMS may include, for certain stationary sources, a) a diluent (O_2) monitor (which must meet its own performance specifications: 40 CFR part 60, Appendix B, Performance Specification 3), b) flow monitoring equipment to allow measurement of the dry volume of stack effluent sampled, and c) an automatic sampling system.

This performance specification requires site specific calibration of the PM CEMS' response against manual gravimetric method measurements. The range of validity of the response calibration is restricted to the range of particulate mass loadings used to develop the calibration relation. Further, if conditions at the facility change (i.e., changes in emission control system or fuel type), then a new response calibration is required. Since the validity of the response calibration may be affected by changes in the properties of the particulate, such as density, index of refraction, and size distribution, the limitations of the CEMS used should be evaluated with respect to these possible changes on a site specific basis.

This specification is not designed to evaluate the installed CEMS' performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS' performance. The source owner or operator, however, is responsible to properly calibrate, maintain, and operate the CEMS. To evaluate the CEMS' performance, the Administrator may require, under Section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test. See Sec. 60.13 (c) and "Quality Assurance Requirements For Particulate Matter Continuous Emission Monitoring Systems Used For Compliance Determination."

1.2 Principle. Installation and measurement location specifications, performance specifications, test procedures, and data reduction procedures are included in this specification. Reference method tests and calibration drift tests are conducted to determine conformance of the CEMS with the specification.

2. *Definitions*

2.1 Continuous Emission Monitoring System (CEMS). The total equipment required for the determination of particulate matter mass concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the CEMS used for one or more of the following: sample acquisition, sample transport, and sample conditioning, or protection of the monitor from the effects of the stack effluent.

2.1.2 Pollutant Analyzer. That portion of the CEMS that senses the particulate matter concentration and generates a proportional output.

2.1.3 Diluent Analyzer (if applicable). That portion of the CEMS that senses the diluent gas (O_2) and generates an output proportional to the gas concentration.

2.1.4 Data Recorder. That portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.

2.2 Point CEMS. A CEMS that measures particulate matter mass concentrations either at a single point or along a path equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section.

2.3 Path CEMS. A CEMS that measures particulate matter mass concentrations along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

2.4 Span Value. The upper limit of the CEMS measurement range.

2.5 Confidence Interval. The interval with upper and lower limits within which the CEMS response calibration relation lies with a given level of confidence.

2.6 Tolerance Interval. The interval with upper and lower limits within which are contained a specified percentage of the population with a given level of confidence.

2.7 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.8 Zero Drift (ZD). The difference in the CEMS output readings for zero input after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.9 Representative Results. Defined by the reference method test procedure defined in this specification.

2.10 Response Time. The time interval between the start of a step change in the system input and the time when the pollutant analyzer output reaches 95 percent of the final value.

2.11 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross sectional area.

2.12 Batch Sampling. Batch sampling refers to the technique of sampling the stack effluent continuously and concentrating the pollutant in some capture medium. Analysis is performed periodically after sufficient time has elapsed to concentrate the pollutant to levels detectable by the analyzer.

2.13 Calibration Standard. Calibration standards produce a known and unchanging response when presented to the pollutant analyzer portion of the CEMS, and are used to calibrate the drift or response of the analyzer.

3. *Installation and Measurement Location Specifications*

3.1 The CEMS Installation and measurement location. Install the CEMS at an accessible location downstream of all pollution control equipment where the particulate matter mass concentrations measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility. Then select representative measurement points or paths for monitoring in locations that the CEMS will meet the calibration requirements (see Section 7). If the cause of failure to meet the calibration requirements is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated.

Measurement locations and points or paths that are most likely to provide data that will meet the calibration requirements are listed below.

3.1.1 Measurement Location. The measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1.

3.1.2 Point CEMS. The measurement point should be (1) no less than 1.0 meter from the stack or duct wall or (2) within or centrally located over the centroidal area of the stack or duct cross section. Selection of traverse points to determine the representativeness of the measurement location should be made according to 40 CFR part 60, Appendix A, Method 1, Section 2.2 and 2.3.

3.1.3 Path CEMS. The effective measurement path should be (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross sectional area, or (3) be centrally located over any part of the centroidal area.

3.1.4 Sampling Requirement for Saturated Flue Gas. If the CEMS is to be installed downstream of a wet air pollution control system such that the flue gases are saturated with water, then the CEMS must isokinetically extract and heat a sample of the flue gas for measurement so that the pollutant analyzer portion of the CEMS measures only dry particulate. Heating shall be to a temperature above the water condensation temperature of the extracted gas and shall be maintained at all points in the sample line, from where the flue gas is extracted to and including the pollutant analyzer. Performance of a CEMS design configured in this manner must be documented by the CEMS manufacturer.

3.2 Reference Method (RM) Measurement Location and Traverse Points. The RM measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The RM and CEMS locations need not be the same, however the difference may contribute to failure of the CEMS to pass the RA test, thus they should be as

close as possible without causing interference with one another. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Selection of traverse measurement point locations should be made according to 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3. If the RM traverse line interferes with or is interfered by the CEMS measurements, the line may be displaced up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area.

4. *Performance and Equipment Specifications*

4.1 Span and Data Recorder Scale.

4.1.1 Span. The span of the instrument shall be three times the applicable emission limit. The span value shall be documented by the CEMS manufacturer with laboratory data.

4.1.2 Data Recorder Scale. The CEMS data recorder response range must include zero and a high level value. The high level value must be equal to the span value. If a lower high level value is used, the CEMS must have the capability of providing multiple outputs with different high level values (one of which is equal to the span value) or be capable of automatically changing the high level value as required (up to the span value) such that the measured value does not exceed 95 percent of the high level value.

4.2 CEMS Response Calibration Specifications. The CEMS response calibration relation must meet the following specifications.

4.2.1 Correlation Coefficient. The correlation coefficient shall be ≥ 0.90.

4.2.2 Confidence Interval. The confidence interval (95%) at the emission limit shall be within ±20% of the emission limit value.

4.2.3 Tolerance Interval. The tolerance interval at the emission limit shall have 95% confidence that 75% of all possible values are within ±35% of the emission limit value.

4.3 Calibration Drift. The CEMS design must allow the determination of calibration drift at concentration levels commensurate with the applicable emission standard. The CEMS calibration may not drift or deviate from the reference value (RV) of the calibration standard by more than 2 percent of the reference value. The calibration shall be performed at a point equal to 80 to 120 percent of the applicable emission standard.

4.4 Zero Drift. The CEMS design must allow the determination of calibration drift at the zero level (zero drift). If this is not possible or practicable, the design must allow the zero drift determination to be made at a low level value (zero to 20 percent of the emission limit value). The CEMS zero point shall not drift by more than 2 percent of the emission standard.

4.5 Sampling and Response Time. The CEMS shall sample the stack effluent continuously. Averaging time, the number of measurements in an average, and the averaging procedure for reporting and determining compliance shall conform with that specified in the applicable emission regulation.

4.5.1 Response Time. The response time of the CEMS should not exceed 2 minutes to achieve 95 percent of the final stable value. The response time shall be documented by the CEMS manufacturer.

4.5.2 Response Time for Batch CEMS. The response time requirement of Section 4.5.1 does not apply to batch CEMS. Instead it is required that the sampling time be no longer than one third of the averaging period for the applicable standard. In addition, the delay between the end of the sampling time and reporting of the sample analysis shall be no greater than one hour. Sampling is also required to be continuous except in that the pause in sampling when the sample collection media are changed should be no greater than five percent of the averaging period or five minutes, whichever is less.

5. *Performance Specification Test Procedure*

5.1 Pretest Preparation. Install the CEMS and prepare the RM test site according to the specifications in Section 3, and prepare the CEMS for operation according to the manufacturer's written instructions.

5.2 Calibration and Zero Drift Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the calibration drift (CD) and zero drift (ZD) once each day (at 24-hour intervals) for 7 consecutive days according to the procedure given in Section 6. To meet the requirements of Sections 4.3 and 4.4 none of the CD's or ZD's may exceed the specification. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or manual adjustment of the CEMS took place.

5.3 CEMS Response Calibration Period. Calibrate the CEMS response following the CD test period. Conduct the calibration according to the procedure given in Section 7 while the affected facility is operating at more than 50 percent of normal load, or as specified in the applicable subpart.

6.0 *The CEMS Calibration and Zero Drift Test Procedure*

This performance specification is designed to allow calibration of the CEMS by use of calibration standard that challenges the pollutant analyzer part of the CEMS (and as much of the whole system as possible), but which does not challenge the entire CEMS, including the sampling interface. Satisfactory response of the entire system is covered by the CEMS response calibration requirements.

The CD measurement is to verify the ability of the CEMS to conform to the established CEMS response calibration used for determining the emission concentration. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before the adjustments, or conduct it in such a way that the CD and ZD can be determined.

Conduct the CD and ZD tests at the points specified in Sections 4.3 and 4.4. Record the CEMS response and calculate the CD according to:

$$CD = \frac{\left(R_{CEM} - R_V \right)}{R_V} X\ 100\ , \qquad (1)$$

where CD denotes the calibration drift of the CEMS in percent, R_{CEM} is the CEMS response, and R_V is the reference value of the high level calibration standard. Calculate the ZD according to:

$$ZD = \frac{\left(R_{CEM} - R_V \right)}{R_{EM}} X\ 100\ , \qquad (2)$$

where ZD denotes the zero drift of the CEMS in percent, R_{CEM} is the CEMS response, R_V is the reference value of the low level calibration standard, and R_{EM} is the emission limit value.

7. *CEMS Response Calibration Procedure*

7.1 Sampling Strategy for Response Calibration. The CEMS response calibration is carried out in order to verify and calibrate the performance of the entire CEMS system, including the sampling interface, by comparison to RM measurements. Conduct the RM measurements in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneously, the diluent and moisture measurements that are taken within a 30- to 60-minute period, which includes the pollutant measurements, may be used to calculate dry pollutant concentration.

7.2 Correlation of RM and CEMS Data. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period of each run (including the exact time of day) in the CEMS data log. Correlate the CEMS and RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then compare each integrated CEMS value against the corresponding average RM value.

7.3 Number of tests. The CEMS response calibration shall be carried out by making simultaneous CEMS and RM measurements at three (or more) different levels of particulate mass concentrations. Three (or more) sets of measurements shall be obtained at each level. A total of at least fifteen measurements shall be obtained. The different levels of particulate mass concentration should be obtained by varying the process conditions as much as the process allows within the range of normal operation. Alternatively, emission levels may be varied by adjusting the particulate control system. It is recommended that the CEMS be calibrated over PM levels ranging from a minimum normal level to a level roughly twice the emission limit, as this will provide the smallest confidence interval bounds on the calibration relation at the emission limit level.

7.4 Reference Methods. Unless otherwise specified in an applicable subpart of the regulations, Method 3B, or its approved alternative, is the reference method for diluent (O_2) concentration. Unless otherwise specified in an applicable subpart of the regulations, Method 5 (40 CFR Part 60, Appendix A), or its approved alternative, is the reference method for particulate

matter mass concentration.

7.5 Calculations. Summarize the results on a data sheet. An example is shown is shown in Figure 2-2 of 40 CFR part 60, Appendix B, Performance Specification 2. Calculate the calibration relation, correlation coefficient, and confidence and tolerance intervals using the equations in Section 8.

8. *Equations*

8.1 Linear Calibration Relation. A linear calibration relation may be calculated from the calibration data by performing a linear least squares regression. The CEMS data are taken as the *x* values, and the reference method data as the *y* values. The calibration relation, which gives the predicted mass emission, $\hat{y}$, based on the CEMS response *x*, is given by

$$\hat{y} = a \cdot x + b \tag{3}$$

where:

$$a = \frac{S_{xy}}{S_{xx}} \tag{4}$$

and

$$b = \overline{y} - a \cdot \overline{x} \tag{5}$$

The mean values of the data sets are given by

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \ , \ \bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i \tag{6}$$

where x_i and y_i are the absolute values of the individual measurements and n is the number of data points. The values S_{xx}, S_{yy}, and S_{xy} are given by

$$S_{xx} = \sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2 , \ S_{yy} = \sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2 , \ S_{xy} = \sum_{i=1}^{n}\left(x_i - \bar{x}\right)\cdot\left(y_i - \bar{y}\right) \tag{7}$$

from which the scatter of y values about the regression line (calibration relation) s_L can be determined:

$$s_L = \sqrt{\frac{S_{yy}}{n-2}\left(1 - \frac{S_{xy}^2}{S_{xx}\cdot S_{yy}}\right)} \tag{8}$$

The two-sided confidence interval y_c for the predicted concentration $\hat{y}$ at point x is given by

$$y_c = \hat{y} \pm t_f \cdot s_L \sqrt{\frac{1}{n} + \frac{\left(x - \bar{x}\right)^2}{S_{xx}}} , \ with \ f = n - 2 \tag{9}$$

The two-sided tolerance interval y_t for the regression line is given by

$$y_T = \hat{y} \pm k_T \cdot s_L \tag{10}$$

at the point x with $k_T = u_{n'} \cdot v_f$ and $f = n - 2$, where

$$n' = \frac{n}{1 + \frac{n\cdot\left(x - \bar{x}\right)^2}{S_{xx}}} \ , \ n' \geq 2. \tag{11}$$

The tolerance factor $u_{n'}$ for 75% of the population is given in Table I as a function of n'. The factor v_f as a function of f is also given in Table I as well as the t-factor at the 95% confidence level.

The correlation coefficient r may be calculated from

$$r = a\sqrt{\frac{S_{xx}}{S_{yy}}} \tag{12}$$

TABLE I: Factors for Calculation of Confidence and Tolerance Intervals

f	t_f	v_f	n'	$u_{n'}(75)$
7	2.365	1.7972	7	1.233
8	2.306	1.7110	8	1.223
9	2.262	1.6452	9	1.214
10	2.228	1.5931	10	1.208
11	2.201	1.5506	11	1.203
12	2.179	1.5153	12	1.199
13	2.160	1.4854	13	1.195
14	2.145	1.4597	14	1.192
15	2.131	1.4373	15	1.189
16	2.120	1.4176	16	1.187
17	2.110	1.4001	17	1.185
18	2.101	1.3845	18	1.183
19	2.093	1.3704	19	1.181
20	2.086	1.3576	20	1.179
21	2.080	1.3460	21	1.178
22	2.074	1.3353	22	1.177
23	2.069	1.3255	23	1.175
24	2.064	1.3165	24	1.174
25	2.060	1.3081	25	1.173

8.2 Quadratic Calibration Relation. In some cases a quadratic regression will provide a better fit to the calibration data than a linear regression. If a quadratic regression is used to determine a calibration relation, a test to determine if the quadratic regression gives a better fit to the data than a linear regression must be performed, and the relation with the best fit must be used.

8.2.1 Quadratic Regression. A least-squares quadratic regression gives the best fit coefficients b_0, b_1, and b_2 for the calibration relation:

$$\hat{y} = b_0 + b_1 x + b_2 x^2 \qquad \textbf{(13)}$$

The coefficients b_0, b_1, and b_2 are determined from the solution to the matrix equation **Ab**=**B** where:

$$\boldsymbol{A} = \begin{bmatrix} n & S_1 & S_2 \\ S_1 & S_2 & S_3 \\ S_2 & S_3 & S_4 \end{bmatrix}, \qquad \boldsymbol{b} = \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix}, \qquad \boldsymbol{B} = \begin{bmatrix} S_5 \\ S_6 \\ S_7 \end{bmatrix},$$

and

$$S_1 = \sum_{i=1}^{n} (x_i), \quad S_2 = \sum_{i=1}^{n} (x_i^2), \quad S_3 = \sum_{i=1}^{n} (x_i^3), \quad S_4 = \sum_{i=1}^{n} (x_i^4),$$

$$S_5 = \sum_{i=1}^{n} y_i, \quad S_6 = \sum_{i=1}^{n} (x_i y_i), \quad S_7 = \sum_{i=1}^{n} (x_i^2 y_i). \qquad \textbf{(14)}$$

The solutions to b_0, b_1, and b_2 are:

$$b_0 = (S_5 \cdot S_2 \cdot S_4 + S_1 \cdot S_3 \cdot S_7 + S_2 \cdot S_6 \cdot S_3 - S_7 \cdot S_2 \cdot S_2 - S_3 \cdot S_3 \cdot S_5 - S_4 \cdot S_6 \cdot S_1) / \det A \quad \textbf{(15)}$$

$$b_1 = (n \cdot S_6 \cdot S_4 + S_5 \cdot S_3 \cdot S_2 + S_2 \cdot S_1 \cdot S_7 - S_2 \cdot S_6 \cdot S_2 - S_7 \cdot S_3 \cdot n - S_4 \cdot S_1 \cdot S_5) / \det A \quad \textbf{(16)}$$

$$b_2 = (n \cdot S_2 \cdot S_7 + S_1 \cdot S_6 \cdot S_2 + S_5 \cdot S_1 \cdot S_3 - S_2 \cdot S_2 \cdot S_5 - S_3 \cdot S_6 \cdot n - S_7 \cdot S_1 \cdot S_1) / \det A \quad \textbf{(17)}$$

where:

$$\det A = n \cdot S_2 \cdot S_4 + S_1 \cdot S_3 \cdot S_2 + S_2 \cdot S_1 \cdot S_3 - S_2 \cdot S_2 \cdot S_2 - S_3 \cdot S_3 \cdot S_2 - S_4 \cdot S_1 \cdot S_1 \quad \textbf{(18)}$$

8.2.2 Confidence Interval. For any positive value of x, the confidence interval is given by:

$$y_{CI} = \hat{y} \pm t_f \cdot s_Q \sqrt{\Delta} \quad \textbf{(19)}$$

where:

$f = n\text{-}3$,
t_f is given in Table I,

$$s_Q = \sqrt{\frac{1}{n-3} \sum_{i=1}^{n} \left(\hat{y}_i - y_i\right)^2}, \text{ and} \quad \textbf{(20)}$$

$$\Delta = C_0 + 2\,C_1\,x + \left(2\,C_2 + C_3\right)x^2 + 2\,C_4\,x^3 + C_5\,x^4 \,. \quad \textbf{(21)}$$

The C coefficients are given below:

$$C_0 = \frac{S_2 \cdot S_4 - S_3^2}{D}, \quad C_1 = \frac{S_3 \cdot S_2 - S_1 \cdot S_4}{D}, \quad C_2 = \frac{S_1 \cdot S_3 - S_2^2}{D},$$

$$C_3 = \frac{n S_4 - S_2^2}{D}, \quad C_4 = \frac{S_1 \cdot S_2 - n S_3}{D}, \quad C_5 = \frac{n S_2 - S_1^2}{D}. \qquad \textbf{(22)}$$

where

$$D = n\left(S_2 \cdot S_4 - S_3^2\right) + S_1\left(S_3 \cdot S_2 - S_1 \cdot S_4\right) + S_2\left(S_1 \cdot S_3 - S_2^2\right). \qquad \textbf{(23)}$$

8.2.3 Tolerance Interval. For any positive value of x, the tolerance interval is given by:

$$y_{TI} = \hat{y} \pm k_T \cdot s_Q, \qquad \textbf{(24)}$$

where:

$k_T = u_{n'} \cdot v_f$ with $f = n\text{-}3$, and **(25)**

$n' = 1/\Delta$ with $n' \geq 2$. **(26)**

The v_f and $u_{n'}$ factors can also be found in Table I.

8.3 Test to Determine Best Regression Fit. The test to determine if the fit using a quadratic regression is better than the fit using a linear regression is based on the values of s calculated in the two formulations. If s_L denotes the value of s from the linear regression and s_Q the value of s from the quadratic regression, then the quadratic regression gives a better fit at the 95% confidence level if the following relationship is fulfilled:

$$\frac{(n-2) \cdot s_L^2 - (n-3) \cdot s_Q^2}{s_Q^2} > F_f \qquad \textbf{(27)}$$

with $f = n\text{-}3$ and the value of F_f at the 95% confidence level as a function of f taken from Table II below.

Table II: Values for F_f.

f	F_f	f	F_f
1	161.4	16	4.49
2	18.51	17	4.45
3	10.13	18	4.41
4	7.71	19	4.38
5	6.61	20	4.35
6	5.99	22	4.30
7	5.59	24	4.26
8	5.32	26	4.23
9	5.12	28	4.20
10	4.96	30	4.17
11	4.84	40	4.08
12	4.75	50	4.03
13	4.67	60	4.00
14	4.60	80	3.96
15	4.54	100	3.94

9. *Reporting*

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any) summarize in tabular form the results of the CD tests and the CEMS response calibration. Include all data sheets, calculations, and records of CEMS response necessary to substantiate that the performance of the CEMS met the performance specifications.

The CEMS measurements shall be reported to the agency in units of mg/m^3 on a dry basis, corrected to 20°C and 7 percent O_2.

10. *Bibliography*

1. 40 CFR part 60, Appendix B, "Performance Specification 2 - Specifications and Test Procedures for SO_2 and NO_x Continuous Emission Monitoring Systems in Stationary Sources."

2. 40 CFR part 60, Appendix B, "Performance Specification 1 - Specification and Test Procedures for Opacity Continuous Emission Monitoring Systems in Stationary Sources."

3. 40 CFR part 60, Appendix A, "Method 1 - Sample and Velocity Traverses for Stationary Sources."

4. 40 CFR part 266, Appendix IX, Section 2, "Performance Specifications for Continuous Emission Monitoring Systems."

5. ISO 10155, “Stationary Source Emissions - Automated Monitoring of Mass Concentrations of Particles: Performance Characteristics, Test Procedures, and Specifications,” available from ANSI.

6. G. Box, W. Hunter, J. Hunter, *Statistics for Experimenters* (Wiley, New York, 1978).

7. M. Spiegel, *Mathematical Handbook of Formulas and Tables* (McGraw-Hill, New York, 1968).15

APPENDIX B

PERFORMANCE SPECIFICATION FOR MERCURY CEMS

PERFORMANCE SPECIFICATION 12 -- Specifications and test procedures for total mercury continuous monitoring systems in stationary sources

1. *Applicability and Principle*

1.1 Applicability. This specification is to be used for evaluating the acceptability of total mercury continuous emission monitoring systems (CEMS) at the time of or soon after installation and whenever specified in the regulations. The CEMS must be capable of measuring the total concentration (regardless of speciation) of both vapor and solid phase mercury. The CEMS may include, for certain stationary sources, a) a diluent (O_2) monitor (which must meet its own performance specifications: 40 CFR part 60, Appendix B, Performance Specification 3), b) flow monitoring equipment to allow measurement of the dry volume of stack effluent sampled, and c) an automatic sampling system.

This specification is not designed to evaluate the installed CEMS' performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS' performance. The source owner or operator, however, is responsible to properly calibrate, maintain, and operate the CEMS. To evaluate the CEMS' performance, the Administrator may require, under Section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test.

1.2 Principle. Installation and measurement location specifications, performance specifications, test procedures, and data reduction procedures are included in this specification. Reference method tests, calibration error tests, and calibration drift tests, and interferant tests are conducted to determine conformance of the CEMS with the specification. Calibration error is assessed with standards for elemental mercury (Hg(0)) and mercuric chloride (HgCl2). The ability of the CEMS to provide a measure of total mercury (regardless of speciation and phase) at the facility at which it is installed is demonstrated by comparison to manual reference method measurements.

2. *Definitions*

2.1 Continuous Emission Monitoring System (CEMS). The total equipment required for the determination of a pollutant concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the CEMS used for one or more of the following: sample acquisition, sample transport, and sample conditioning, or protection of the monitor from the effects of the stack effluent.

2.1.2 Pollutant Analyzer. That portion of the CEMS that senses the pollutant concentration(s) and generates a proportional output.

2.1.3 Diluent Analyzer (if applicable). That portion of the CEMS that senses the diluent

gas (O_2) and generates an output proportional to the gas concentration.

2.1.4 Data Recorder. That portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.

2.2 Point CEMS. A CEMS that measures the pollutant concentrations either at a single point or along a path equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section.

2.3 Path CEMS. A CEMS that measures the pollutant concentrations along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

2.4 Span Value. The upper limit of a pollutant concentration measurement range defined as twenty times the applicable emission limit. The span value shall be documented by the CEMS manufacturer with laboratory data.

2.5 Relative Accuracy (RA). The absolute mean difference between the pollutant concentration(s) determined by the CEMS and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

2.6 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.7 Zero Drift (ZD). The difference in the CEMS output readings for zero input after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.8 Representative Results. Defined by the RA test procedure defined in this specification.

2.9 Response Time. The time interval between the start of a step change in the system input and the time when the pollutant analyzer output reaches 95 percent of the final value.

2.10 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross sectional area.

2.11 Batch Sampling. Batch sampling refers to the technique of sampling the stack effluent continuously and concentrating the pollutant in some capture medium. Analysis is performed periodically after sufficient time has elapsed to concentrate the pollutant to levels detectable by the analyzer.

2.12 Calibration Standard. Calibration standards consist of a known amount of pollutant that is presented to the pollutant analyzer portion of the CEMS in order to calibrate the drift or response of the analyzer. The calibration standard may be, for example, a solution containing a known concentration, or a filter with a known mass loading or composition.

2.13 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration generated by a calibration source when the entire CEMS, including the sampling interface) is challenged. A CE test procedure is performed to document

the accuracy and linearity of the CEMS over the entire measurement range.

3. *Installation and Measurement Location Specifications*

3.1 The CEMS Installation and measurement location. Install the CEMS at an accessible location downstream of all pollution control equipment where the mercury concentration measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility. Then select representative measurement points or paths for monitoring in locations that the CEMS will pass the RA test (see Section 7). If the cause of failure to meet the RA test is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated.

Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

3.1.1 Measurement Location. The measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1.

3.1.2 Point CEMS. The measurement point should be (1) no less than 1.0 meter from the stack or duct wall or (2) within or centrally located over the centroidal area of the stack or duct cross section. Selection of traverse points to determine the representativeness of the measurement location should be made according to 40 CFR part 60, Appendix A, Method 1, Section 2.2 and 2.3.

3.1.3 Path CEMS. The effective measurement path should be (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross sectional area, or (3) be centrally located over any part of the centroidal area.

3.2 Reference Method (RM) Measurement Location and Traverse Points. The RM measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The RM and CEMS locations need not be the same, however the difference may contribute to failure of the CEMS to pass the RA test, thus they should be as close as possible without causing interference with one another. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Selection of traverse measurement point locations should be made according to 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3. If the RM traverse line interferes with or is interfered by the CEMS measurements, the line may be displaced up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area.

4. *Performance and Equipment Specifications*

4.1 Data Recorder Scale. The CEMS data recorder response range must include zero and a high level value. The high level value must be equal to the span value. If a lower high level value is used, the CEMS must have the capability of providing multiple outputs with different high level values (one of which is equal to the span value) or be capable of automatically changing the high level value as required (up to the span value) such that the measured value does not exceed 95 percent of the high level value.

4.2 Relative Accuracy (RA). The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of the emission standard, or 10 percent of the applicable standard, whichever is greater.

4.3 Calibration Error. Calibration error is assessed using standards for Hg(0) and HgCl2. The mean difference between the indicated CEMS concentration and the reference concentration value for each standard at all three test levels listed below shall be no greater than ±15 percent of the reference concentration at each level.

4.3.1 Zero Level. Zero to twenty (0 - 20) percent of the emission limit.

4.3.2 Mid-Level. Forty to sixty (40 - 60) percent of the emission limit.

4.3.3 High-Level. Eighty to one-hundred and twenty (80 - 120) percent of the emission limit.

4.4 Calibration Drift. The CEMS design must allow the determination of calibration drift of the pollutant analyzer at concentration levels commensurate with the applicable emission standard. The CEMS calibration may not drift or deviate from the reference value (RV) of the calibration standard by more than 10 percent of the emission limit. The calibration shall be performed at a level equal to 80 to 120 percent of the applicable emission standard. Calibration drift shall be evaluated for elemental mercury only.

4.5 Zero Drift. The CEMS design must allow the determination of calibration drift at the zero level (zero drift). The CEMS zero point shall not drift by more than 5 percent of the emission standard.

4.6 Sampling and Response Time. The CEMS shall sample the stack effluent continuously. Averaging time, the number of measurements in an average, and the averaging procedure for reporting and determining compliance shall conform with that specified in the applicable emission regulation.

4.6.1 Response Time. The response time of the CEMS should not exceed 2 minutes to achieve 95 percent of the final stable value. The response time shall be documented by the CEMS manufacturer.

4.6.2 Waiver from Response Time Requirement. A source owner or operator may receive a waiver from the response time requirement for instantaneous, continuous CEMS in section 4.5.1 from the Agency if no CEM is available which can meet this specification at the time of purchase of the CEMS.

4.6.3 Response Time for Batch CEMS. The response time requirement of Section 4.5.1 does not apply to batch CEMS. Instead it is required that the sampling time be no longer than

one third of the averaging period for the applicable standard. In addition, the delay between the end of the sampling time and reporting of the sample analysis shall be no greater than one hour. Sampling is also required to be continuous except in that the pause in sampling when the sample collection media are changed should be no greater than five percent of the averaging period or five minutes, whichever is less.

4.7 CEMS Interference Response. While the CEMS is measuring the concentration of mercury in the high-level calibration sources used to conduct the CE test the gaseous components (in nitrogen) listed in Table I shall be introduced into the measurement system either separately or in combination. The interference test gases must be introduced in such a way as to cause no change in the mercury or mercuric chloride calibration concentration being delivered to the CEMS. The concentrations listed in the table are the target levels at the sampling interface of the CEMS based on the known cylinder gas concentrations and the extent of dilution (see Section 9). Interference is defined as the difference between the CEMS response with these components present and absent. The sum of the interferences must be less than 10 percent of the emission limit value. If this level of interference is exceeded, then corrective action to eliminate the interference(s) must be taken.

Table I
Interference Test Gas Concentrations in Nitrogen

Gas	**Concentration**
Carbon Monoxide	500 ± 50 ppm
Carbon Dioxide	10 ± 1 percent
Oxygen	20.9 ± 1 percent
Sulfur Dioxide	500 ± 50 ppm
Nitrogen Dioxide	250 ± 25 ppm
Water Vapor	25 ± 5 percent
Hydrogen Chloride (HCl)	50 ± 5 ppm
Chlorine (Cl2)	10 ± 1 ppm

4.8 Calibration Source Requirements for Assessment of Calibration Error. The calibration source must permit the introduction of known (NIST traceable) and repeatable concentrations of elemental mercury (Hg(0)) and mercuric chloride (HgCl2) into the sampling system of the CEMS. The CEMS manufacturer shall document the performance of the calibration source, and submit this documentation and a calibration protocol to the administrator for approval. Determination of CEMS calibration error must then be made in using the approved calibration source and in accordance with the approved protocol.

4.8.1 Design Considerations. The calibration source must be designed so that the flowrate of calibration gas introduced to the CEMS is the same at all three calibration levels specified in Section 4.3 and at all times exceeds the flow requirements of the CEMS.

4.8.2 Calibration Precision. A series of three injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than ±5 percent from the mean of the three injections. Failure to attain this level of precision is an indication of a problem in the calibration system or the CEMS. Any such problem must be identified and corrected before proceeding.

5. *Performance Specification Test Procedure*

5.1 Pretest Preparation. Install the CEMS and prepare the RM test site according to the specifications in Section 3, and prepare the CEMS for operation according to the manufacturer's written instructions.

5.2 Calibration and Zero Drift Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the calibration drift (CD) and zero drift (ZD) once each day (at 24-hour intervals) for 7 consecutive days according to the procedure given in Section 6. To meet the

requirements of Sections 4.4 and 4.5 none of the CD's or ZD's may exceed the specification. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or manual adjustment of the CEMS took place.

5.3 CE Test Period. Conduct a CE test prior to the CD test period. Conduct the CE test according to the procedure given in Section 8.

5.4 CEMS Interference Response Test Period. Conduct an interference response test in conjunction with the CE test according to the procedure given in Section 9.

5.5 RA Test Period. Conduct a RA test following the CD test period. Conduct the RA test according to the procedure given in Section 7 while the affected facility is operating at more than 50 percent of normal load, or as specified in the applicable subpart.

6.0 *The CEMS Calibration and Zero Drift Test Procedure*

This performance specification is designed to allow calibration of the CEMS by use of standard solutions, filters, etc that challenge the pollutant analyzer part of the CEMS (and as much of the whole system as possible), but which do not challenge the entire CEMS, including the sampling interface. Satisfactory response of the entire system is covered by the RA and CE requirements.

The CD measurement is to verify the ability of the CEMS to conform to the established CEMS calibration used for determining the emission concentration. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before the adjustments, or conduct it in such a way that the CD and ZD can be determined.

Conduct the CD and ZD tests at the points specified in Sections 4.4 and 4.5. Record the CEMS response and calculate the CD according to:

$$CD = \frac{\left(R_{CEM} - R_V \right)}{R_V} X\ 100\ , \qquad (1)$$

where CD denotes the calibration drift of the CEMS in percent, R_{CEM} is the CEMS response, and R_V is the reference value of the high level calibration standard. Calculate the ZD according to:

$$ZD = \frac{\left(R_{CEM} - R_V \right)}{R_{EM}} X\ 100\ , \qquad (2)$$

where ZD denotes the zero drift of the CEMS in percent, R_{CEM} is the CEMS response, R_V is the reference value of the low level calibration standard, and R_{EM} is the emission limit value.

7. *Relative Accuracy Test Procedure*

7.1 Sampling Strategy for RA Tests. The RA tests are to verify the initial performance of the entire CEMS system, including the sampling interface, by comparison to

RM measurements. Conduct the RM measurements in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneously, the diluent and moisture measurements that are taken within a 30- to 60-minute period, which includes the pollutant measurements, may be used to calculate dry pollutant concentration.

A measure of relative accuracy at a single level that is detectable by both the CEMS and the RM is required.

In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period of each run (including the exact time of day) in the CEMS data log.

7.2 Correlation of RM and CEMS Data. Correlate the CEMS and RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then compare each integrated CEMS value against the corresponding average RM value.

7.3 Number of tests. Obtain a minimum of three pairs of CEMS and RM measurements. If more than nine pairs of measurements are obtained, then up to three pairs of measurements may be rejected so long as the total number of measurement pairs used to determine the RA is greater than or equal to nine. However, all data, including the rejected data, must be reported.

7.4 Reference Methods. Unless otherwise specified in an applicable subpart of the regulations, Method 3B, or its approved alternative, is the reference method for diluent (O_2) concentration. Unless otherwise specified in an applicable subpart of the regulations, the manual method for multi-metals in 40 CFR part 266, Appendix IX, Section 3.1 (until superseded by SW-846), or its approved alternative, is the reference method for mercury.

7.5 Calculations. Summarize the results on a data sheet. An example is shown is shown in Figure 2-2 of 40 CFR part 60, Appendix B, Performance Specification 2. Calculate the mean of the RM values. Calculate the arithmetic differences between the RM and CEMS output sets, and then calculate the mean of the differences. Calculate the standard deviation of each data set and CEMS RA using the equations in Section 10.

8. *Calibration Error Test Procedure*

8.1 Sampling Strategy. The CEMS calibration error shall be assessed using calibration sources of elemental mercury and mercuric chloride in turn (see Section 4.8 for calibration source requirements). Challenge the CEMS at the measurement levels specified in Section 4.3. During the test, operate the CEMS as nearly as possible in its normal operating mode. The calibration gases should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling.

8.2 Number of tests. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each challenge should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned and a stable output obtained.

8.3 Calculations. Summarize the results on a data sheet. Calculate the mean difference between the CEMS response and the known reference concentration at each measurement point according to equations 5 and 6 of Section 10. The calibration error (CE) at each measurement point is then given by:

$$CE = |d/R_V| X100, \qquad (3)$$

where R_V is the reference concentration value.

9. *Interference Response Test Procedure*

9.1 Test Strategy. Perform the interference response test while the CEMS is being challenged by the high level calibration source for mercury (after the CE determination has been made), and again while the CEMS is being challenged by the high level calibration source for mercuric chloride (after the CE determination has been made). The interference test gases should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling.

9.2 Number of tests. Introduce the interference test gas three times alternately with the high-level calibration gas and record the responses both with and without the interference test gas. The duration of each test should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned and a stable output obtained.

9.3 Calculations. Summarize the results on a data sheet. Calculate the mean difference between the CEMS response with and without the interference test gas by taking the average of the CEMS responses with and without the interference test gas (see equation 5) and then taking the difference (d). The percent interference (I) is then given by:

$$I = |d/R_{HL}| X100, \qquad (4)$$

where R_{HL} is the value of the high-level calibration standard. If the gaseous components of the interference test gas are introduced separately, then the total interference is the sum of the individual interferences.

10. *Equations*

10.1 Arithmetic Mean. Calculate the arithmetic mean of a data set as follows:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i , \qquad (5)$$

where n is equal to the number of data points.

10.1.1 Calculate the arithmetic mean of the difference, d, of a data set, using Equation 5 and substituting d for x. Then

$$d_i = x_i - y_i \,, \tag{6}$$

where x and y are paired data points from the CEMS and RM, respectively.

10.2 Standard Deviation. Calculate the standard deviation (SD) of a data set as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} x_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} x_i\right)^2}{n-1}} \,, \tag{7}$$

10.3 Relative Accuracy (RA). Calculate the RA as follows:

$$RA = \frac{\bar{d} + \frac{t_{0.975}}{\sqrt{n}}(SD)}{\bar{R}_{RM}} \,, \tag{8}$$

where $\bar{d}$ is equal to the arithmetic mean of the difference, d, of the paired CEMS and RM data set, calculated according to Equations 5 and 6, SD is the standard deviation calculated according to Equation 7, $\bar{R}_{RM}$ is equal to either the average of the RM data set, calculated according to Equation 5, or the value of the emission standard, as applicable (see Section 4.2), and $t_{0.975}$ is the t-value at 2.5 percent error confidence, see Table II.

TABLE II
t-Values

n^a	$t_{0.975}$	n^a	$t_{0.975}$	n^a	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

11. *Reporting*

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any) summarize in tabular form the results of the CE, interference response, CD and RA tests. Include all data sheets, calculations, and records of CEMS response necessary to substantiate that the performance of the CEMS met the performance specifications.

The CEMS measurements shall be reported to the agency in units of $\mu g/m^3$ on a dry basis, corrected to 20°C and 7 percent O_2.

12. *Bibliography*

1. 40 CFR Part 60, Appendix B, "Performance Specification 2 - Specifications and Test Procedures for SO_2 and NO_x Continuous Emission Monitoring Systems in Stationary Sources."

2. 40 CFR Part 60, Appendix B, "Performance Specification 1 - Specification and Test Procedures for Opacity Continuous Emission Monitoring Systems in Stationary Sources."

3. 40 CFR Part 60, Appendix A, "Method 1 - Sample and Velocity Traverses for Stationary Sources."

4. 40 CFR Part 266, Appendix IX, Section 2, "Performance Specifications for Continuous Emission Monitoring Systems."

5. Draft Method 29, "Determination of Metals Emissions from Stationary Sources," Docket A-90-45, Item II-B-12, and EMTIC CTM-012.WPF.

6. "Continuous Emission Monitoring Technology Survey for Incinerators, Boilers, and Industrial Furnaces: Final Report for Metals CEM's," prepared for the Office of Solid Waste, U.S. EPA, Contract No. 68-D2-0164 (4/25/94).

7. 40 CFR Part 60, Appendix A, Method 16, “Semicontinuous Determination of

Sulfur Emissions from Stationary Sources."

8. 40 CFR Part 266, Appendix IX, Performance Specification 2.2, "Performance Specifications for Continuous Emission Monitoring of Hydrocarbons for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste."

APPENDIX C

PERFORMANCE SPECIFICATION FOR HCl CEMS

PERFORMANCE SPECIFICATION 13 -- Specifications and test procedures for hydrochloric acid continuous monitoring systems in stationary sources

1. *Applicability and principle*

1.1 Applicability. This specification is to be used for evaluating the acceptability of hydrogen chloride (HCl) continuous emission monitoring systems (CEMS) at the time of or soon after installation and whenever specified in the pertinent regulations. Some source specific regulations require the simultaneous operation of diluent monitors. These may be O_2 or CO_2 monitors.

This specification does not evaluate the performance of installed CEMS over extended periods of time. The specification does not identify specific calibration techniques or other auxiliary procedures that will assess the CEMS performance. Section 114 of the Act authorizes the administrator to require the operator of the CEMS to conduct performance evaluations at times other than immediately following the initial installation.

This specification is only applicable to monitors that unequivocally measure the concentration of HCl in the gas phase. It is not applicable to CEMS that do not measure gas phase HCl, per se, or CEMS that may have significant interferences. The Administrator believes that HCl CEMS must measure the concentration of gaseous HCl thereby eliminating interferences from volatile inorganic and/or organic chlorinated compounds. CEMS that are based upon infrared measurement techniques, non-dispersive infrared (NDIR), gas filter correlation infrared (GFC-IR) and Fourier Transform infrared (FTIR) are examples of acceptable measurement techniques. Other measurement techniques that unequivocally measure the concentration of HCl in the gas phase may also be acceptable.

1.2 Principle. This specification includes installation and measurement location specifications, performance and equipment specifications, test procedures, and data reduction procedures. This specification also provides definitions of acceptable performance.

This specification stipulates that audit gas tests and calibration drift tests be used to assess the performance of the CEMS. The determination of the accuracy with which the CEMS measures HCl is measured by challenging the CEMS with audit gas of known concentration. There is no absolute determination of interference with the measurement of gas phase HCl with other constituents in the stack gases.

2. *Definitions*

2.1 Continuous Emission Monitoring System. The total equipment required for the determination of the concentration of a gas or its emission rate. The CEMS consist of the

following subsystems:

2.1.1 Sample Interface. That portion of the CEMS used for one or more of the following: sample acquisition, sample transportation, sample conditioning, and protection of the monitor from the effects of the stack effluent.

2.1.2 Pollutant Analyzer. That portion of the CEMS that senses the pollutant gas and generates an output that is proportional to the gas concentration.

2.1.3 Diluent Analyzer. That portion of the CEMS that senses the concentration of the diluent gas (e.g., CO_2 or O_2) and generates an output that is proportional to the concentration of the diluent.

2.1.4 Data Recorder. That portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may include automatic data reduction capabilities.

2.2 Point CEMS. A CEMS that measures the gas concentration either at a single point or along a path equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section. The equivalent diameter must be determined as specified in Appendix A, Method 1 of this Part.

2.3 Path CEMS. A CEMS that measures the gas concentration along a path greater than 10 percent of the equivalent diameter (Appendix A, Method 1) of the stack of duct cross section.

2.4 Span Value. The upper limit of a gas concentration measurement range specified for affected source categories in the applicable subpart of the regulations.

2.5 Accuracy. A measurement of agreement between a measured value and an accepted or true value, expressed as the percentage difference between the true and measured values relative to the true value. For these performance specifications, accuracy is checked by conducting a calibration error (CE) test.

2.6 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration of the cylinder gas. A CE test procedure is performed to document the accuracy and linearity of the monitoring equipment over the entire measurement range.

2.7 Calibration Drift. (CD). The difference between the CEMS output and the concentration of the calibration gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.8 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section is no greater than 1 percent of the stack or duct cross-sectional area.

2.9 Representative Results. Defined by the RM test procedure outlined in this specification

3. *Installation and Measurement Location Specifications*

3.1 CEMS Installation and Measurement Locations. The CEMS shall be installed in a location in which measurements representative of the source's emissions can be obtained. The optimum location of the sample interface for the CEMS is determined by a number of factors,

including ease of access for calibration and maintenance, the degree to which sample conditioning will be required, the degree to which it represents total emissions, and the degree to which it represents the combustion situation in the firebox. The location should be as free from in-leakage influences as possible and reasonably free from severe flow disturbances. The sample location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs and at least 0.5 diameter upstream from the exhaust or control device. The equivalent duct diameter is calculated as per 40 CFR part 60, appendix A, method 1, section 2.1. If these criteria are not achievable or if the location is otherwise less than optimum, the possibility of stratification should be investigated as described in section 3.2. The measurement point shall be within the centroidal area of the stack or duct cross section.

3.1.1 Point CEMS It is suggested that the measurement point be (1) no less than 1.0 meter from the stack or duct wall or (2) within or centrally located over the centroidal area of the stack or duct cross section.

3.1.2 Path CEMS. It is suggested that the effective measurement path (1) be totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross-sectional area.

3.2 Stratification Test Procedure. Stratification is defined as a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall. To determine whether effluent stratification exists, a dual probe system should be used to determine the average effluent concentration while measurements at each traverse point are being made. One probe, located at the stack or duct centroid, is used as a stationary reference point to indicate the change in effluent concentration over time. The second probe is used for sampling at the traverse points specified in 40 CFR part 60 appendix A, method 1. The monitoring system samples sequentially at the reference and traverse points throughout the testing period for five minutes at each point.

4. *Performance and Equipment Specifications.*

4.1 Data Recorder Scale. The CEMS data recorder response range must include zero and a high-level value. The high-level value is chosen by the source owner or operator and is defined as follows:

For a CEMS intended to measure an uncontrolled emission (e.g., at the inlet of a scrubber) the high-level value must be between 1.25 and 2.0 times the average potential emission concentration, unless another value is specified in an applicable subpart of the regulations. For a CEMS installed to measure controlled emissions or emissions that are in compliance with an applicable regulation, the high-level value must be between 1.5 times the HCl concentration corresponding to the emission standard level and the span value. If a lower high-level value is used, the operator must have the capability of requirements of the applicable regulations.

The data recorder output must be established so that the high-level value is read between 90 and 100 percent of the data recorder full scale. (This scale requirement may not be applicable

to digital data recorders.) The calibration gas, optical filter or cell values used to establish the data recorder scale should produce the zero and high-level values. Alternatively, a calibration gas, optical filter, or cell value between 50 and 100 percent of the high-level value may be used in place of the high-level value, provided that the data recorder full-scale requirements as described above are met.

The CEMS design must also allow the determination of calibration drift at the zero and high-level values. If this is not possible or practicable, the design must allow these determinations to be conducted at a low-level value (zero to 20 percent of the high-level value) and at a value between 50 and 100 percent of the high-level value.

4.2 Calibration Drift. The CEMS calibration must not drift or deviate from the reference value of the gas cylinder, gas cell, or optical filter by more than 2.5 percent of the span value. If the span value of the CEMS is 20 ppm or less then the calibration drift must be less than 0.5 parts per million, for 6 out of 7 test days.

If the CEMS includes both HCl and diluent monitors, the calibration drift must be determined separately for each in terms of concentrations (see PS 3 for the diluent specifications).

4.3 Calibration Error (CE). Calibration error is assessed using EPA protocol 1 cyinder gases for HCl . The mean difference between the indicated CEMS concentration and the reference concentration value for each standard at all three test levels indicated below shall be no greater than 15 percent of the refernce concentration at each level.

4.3.1 Zero Level. Zero to twenty (0 - 20) percent of the emission limit.

4.3.2 Mid Level. Forty to sixty (40 - 60) percent of the emission limit.

4.3.3 High Level. Eighty to one-hundred and twenty (80 - 120) percent of the emission limit.

4.4 CEMS Interference Response Test. Introduce the gaseous components listed in Table PS HCl-1 into the measurement system of the CEMS, while the measurement system is measuring the concentration of HCl in a calibration gas. These components may be introduced separately or as gas mixtures. Adjust the HCl calibration gas and gaseous component flow rates so as to maintain a constant concentration of HCl in the gas mixture being introduced into the measurement system. Record the change in the measurement system response to the HCl on a form similar to Figure PS HCl-1. If the sum of the interferences is greater than 2 percent of the applicable span concentration, take corrective action to eliminate the interference.

Table PS HCl-1
Interference Test Gases Concentrations

Gas	Concentration
Carbon Monoxide	500 ± 50 ppm
Carbon Dioxide	10 ± 1 percent
Oxygen	20.9 ±1 percent
Sulfur Dioxide	500 ± 50 ppm
Water Vapor	25 ± 5 percent
Nitrogen Dioxide	250 ±25 ppm

Figure PS HCl -1
Interference Response

Date of Test _____
Analyzer Type _____
Serial Number _____
HCl Calibration Gas Concentration

Test Gas	Concentration	Analyzer Response	Analyzer Error	Percent of Span

Conduct an interference response test of each analyzer prior to its initial use in the field. Thereafter, re-check the measurement system if changes are made in the instrumentation that could alter the interference response, e.g., changes in the type of gas detector.

4.5 Sampling and Response Time. The CEMS shall sample the stack effluent continuously. Averaging time, the number of measurements in an average, and the averaging procedure for reporting and determining compliance shall conform with that specified in the applicable emission regulation.

4.5.1 Response Time. The response time of the CEMS should not exceed 2 minutes to achieve 95 percent of the final stable value. The response time shall be documented by the CEMS manufacturer.

4.5.2 Waiver from Response Time Requirement. A source owner or operator may receive a waiver from the response time requirement for instantaneous, continuous CEMS in section 4.5.1 from the Agency if no CEM is available which can meet this specification at the time of purchase of the CEMS.

4.5.3 Response Time for Batch CEMS. The response time requirement of Section 4.5.1 does not apply to batch CEMS. Instead it is required that the sampling time be no longer than one third of the averaging period for the applicable standard. In addition, the delay between the end of the sampling time and reporting of the sample analysis shall be no greater than one hour. Sampling is also required to be continuous except in that the pause in sampling when the sample collection media are changed should be no greater than five percent of the averaging period or five minutes, whichever is less.

5. *Performance Specification Test Procedure*

5.1 Pretest Preparation. Install the CEMS, prepare the RM test site according to the specifications in Section 3, and prepare the CEMS for operation according to the manufacturer's written instructions.

5.2 Calibration Drift Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the calibration drift (CD) once each day (at 24-hour intervals) for 7 consecutive days. according to the procedure given in Section 6. The CD may not exceed the specification given in Section 4.2.

5.3 CE Test Period. Conduct a CE test prior to the CD test period. Conduct the CE test according to the procedure given in section 7.

6. *The CEMS Calibration Drift Test Procedure*

The CD measurement is to verify the ability of the CEMS to conform to the established CEMS calibration used for determining the emission concentration or emission rate. Therefore, if periodic automated or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined.

Conduct the CD test at the two points specified in Section 4.1. Introduce the reference gases, gas cells or optical filters (these need not be certified) to the CEMS. Record the CEMS response and subtract this value from the reference value (see the example data sheet in Figure 2-1).

7. *Calibration Error Test Procedure*

7.1 Sampling Strategy. The CEMS calibration error shall be assessed using the calibration source specified in Section 4.3. Challenge the CEMS at the measurement levels specified in Section 4.3. During the test, operate the CEMS as nearly as possible in its normal operating mode. The calibration gases should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling.

7.2 Number of tests. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each challenge should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned and a stable output obtained.

7.3 Calculations. Summarize the results on a data sheet. Calculate the mean difference between the CEMS response and the known reference concentration at each measurement point according to equations 1 and 2 of Section 8. The calibration error (CE) at each measurement point is then given by:

$$CE = |d/R_v| X100, \qquad (1)$$

where R_V is the reference concentration value.

8. *Equations*

8.1 Arithmetic Mean. Calculate the arithmetic mean of the difference, d, of a data set as follows:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad (2)$$

Where:

n = number of data points.

$$\sum_{i=1}^{n} d_i = \text{Algebraic sum of the individual differences } d_i$$

When the mean of the differences of pairs of data is calculated, be sure to correct the data for moisture, if applicable.

9. *Reporting*

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any) summarize in tabular form the results of the CD tests and the relative accuracy tests or alternative RA procedure as appropriate. Include all data sheets, calculations, charts (records of CEMS responses), cylinder gas concentration certifications (if applicable), necessary to substantiate that the performance of the CEMS met the performance specifications.