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Continuous Emission Monitoring Systems for Non-criteria Pollutants

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Center for Environmental Research Information
National Risk Management Research Laboratory
Office of Research and Development
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Notice

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Chapter 1
Introduction

1.1 Background and Objectives of the Handbook

This Handbook provides a description of the methods used to continuously monitor non-criteria pollutants emitted from stationary sources. The Handbook contains a review of current regulatory programs, the state-of-the-art sampling system design, analytical techniques, and the use of computer systems for data acquisition and predictive monitoring. The Handbook is intended for those in industry or in government who are charged with implementing a continuous emission monitoring (CEM) program for this wider range of air pollutants.

In 1979, a Technology Transfer handbook was prepared on the topic of CEM systems to provide the detailed information necessary for developing continuous monitoring programs at stationary sources (EPA, 1979). This information was updated in subsequent publications (EPA, 1991 and Jahnke, 1993); however, the original Handbook and these later materials focused on the monitoring of the criteria pollutants such as sulfur dioxide (SO_2) and the oxides of nitrogen (NO_x). Due to the successes of earlier CEM programs, requirements for CEM have been and are being extended to cover a wider range of pollutant categories such as volatile organic compounds (VOCs) and hazardous air pollutants (HAPs).

Although the installation of monitoring systems is most frequently initiated through regulation, the use of these systems for optimizing and improving process operations has proven to be an important benefit for many companies. When accurate emissions data are available, plant operators are provided with the baseline information necessary to control operations or to change operational practices. The net benefit for both industry and the public is to improve operational efficiencies with a consequent reduction of emissions to the atmosphere.

1.2 Evolution of Continuous Emission Monitoring - Regulatory Programs

Federal CEM requirements were originally established in the U.S. for tracking the performance of air pollution control equipment under the mandates of the EPA New Source Performance Standards (NSPS). Data obtained under this program are reported when emission standards are exceeded. These "excess emission reports" are then used to determine if control equipment performance warrants conducting an inspection or a reference method test (40 CFR 60 Appendix A, USEPA, 1996a) to determine whether the source is in compliance with its emission standards. This program began in the middle 1970's and after a number of years of experience, enough confidence was achieved in CEM systems to use the resultant data directly for the enforcement of emission standards (McCoy, 1986).

To withstand the rigors of litigation, CEM quality assurance programs became necessary to establish the continuing validity of the data. Subsequently, quality assurance requirements for CEM systems (40 CFR 60 Appendix F, USEPA, 1996b) were promulgated in 1986 for sources where the systems are used for monitoring compliance with emissions standards. By the late 1980's, federal experience with electric utilities constructed after 1978 (the Subpart Da sources) and the stringent CEM-based enforcement program of Pennsylvania, indicated that CEM systems could achieve both high levels of accuracy and availability. For SO_2 and NO_x monitoring systems, accuracies of 10%, relative to the EPA Reference Test Methods of 40 CFR 60 Appendix A, were common. System availabilities of 95% were attained for gas measurements and availabilities of 98% for opacity monitors had become achievable in practice.

The encouraging experience of these earlier (and continuing) programs helped to establish CEM as the foundation for the acid rain program of the 1990 Clean Air Act Amendments. In this emissions trading program, emission allowances (one allowance granting the right to emit 1 ton of SO_2 per year) were originally allocated and reserved so that a net reduction of 10,000,000 tons of SO_2 would be realized by the year 2010. Allowances can be viewed as financial instruments that can be bought, sold, traded, etc. CEM systems enter this picture by providing the means of determining who has how many allowances --- how many are used up, and how many are unused

and available for trading. The CEM systems are essentially, the "gold standard" on which the allowance trading program is based (EPA 1991b).

Stringent performance requirements were established (40 CFR 75) for CEM systems used in the acid rain program. As a result of these requirements and the importance of CEM systems for tracking allowances, the systems received greater attention from upper management than in previous programs. Resources were allocated for both purchase and maintenance and responsibility for the systems was given to higher levels of management. After a year of operation of the first phase of the program, relative accuracies of 5 - 6% were common, with corresponding availabilities of 95% or better.

The success of CEM systems at the electric utilities has encouraged their application for monitoring a wider range of pollutants at other types of emissions sources. Monitoring programs are well established at pulp and paper mills, petroleum refineries, municipal waste combustors, hazardous waste incinerators, and cement kilns. At hazardous waste incinerators, stringent operating permits go so far as to require that waste feed be shut off when the monitors indicate that carbon monoxide emission levels are too high or oxygen percentages are too low. Particularly in the case of hazardous waste incineration, continuous monitoring data provide assurances to the public that plant emissions are being controlled continually within safe levels.

The Clean Air Act Amendments of 1990 address two other issues. One is the public concern for the emission of hazardous air pollutants, the so-called "air toxics" (CAAA 1990 - Title III). Title III contains a list of 189 pollutants, principally organic compounds and metals (see Appendix D). Depending upon rules specifying "Maximum Achievable Control Technology" (the so-called "MACT" standards), certain operations likely will be required to monitor the emission of these materials on a continuous basis.

Title VII of the Clean Air Act Amendments refers to the term "enhanced monitoring" (§702(b)(3)), where sources are required to certify that they are in compliance with their emissions limitations. "Enhanced Monitoring" has evolved into the "Compliance Assurance Monitoring" (CAM) rule, where CEM systems or other techniques may be used by the source to track its compliance status.

The air toxics and CAM rules affect a wide variety of emissions sources. Many of these sources are small, relative to the larger industrial sources that have been required to install CEM systems through the NSPS Part 60 or acid rain Part 75 rules. For these smaller sources, arguments often arise that CEM systems are too costly, that the technology is too new, or that extensive evaluation programs need to be conducted before CEM systems can be used for regulatory purposes. However, much is known about CEM systems. With over 25 years of experience both in the United States and Europe, continuous emission monitoring for many pollutants is a mature technology. With the one time upsurge of Acid Rain CEM system sales in the early 1990's, subsequent market pressures have forced CEM system vendors and integrators to reduce costs to remain competitive. In addition to the present knowledge base and market pressures, new technologies are being introduced into this field at a rapid pace. This combination of factors has created an array of options for meeting monitoring requirements for hazardous air pollutants.

1.3 Current Status of Continuous Emission Monitoring - Monitoring Technology

Monitoring pollutant emissions from stationary sources involves two principle functions: 1) extracting or locating a representative sample and 2) analyzing that sample. Monitoring methods in use today are illustrated in Figure 1-1.

Extractive and in-situ methods are used to monitor gas concentrations directly. In the case of extractive systems, gas is withdrawn from the stack, conditioned, and then analyzed. In in-situ systems, gas is not extracted, but is monitored directly in the stack by the analyzer. In the indirect parameter monitoring methods, plant operational or control equipment parameters are correlated to emissions determined by manual or instrument reference methods. To the extent that the parameter method's validity depends on correlated data, representative sampling and analysis are equally as important as in the direct extractive and in-situ measurement methods.

The choice and design of a CEM system depends on both the regulatory requirements and the types of pollutants and/or parameters that are to be monitored. For example, when emissions are reported in kg/hr or tons/year, a pollutant monitor plus a volumetric flow determination are usually necessary. If concentration corrected values are required (such as ppm corrected to 3% O_2 or 12% O_2), then a pollutant monitor plus a diluent monitor (O_2 or CO_2) are required.

Different gases have different properties and some are more amenable to analysis than others. Many well-proven techniques are available for monitoring sulfur

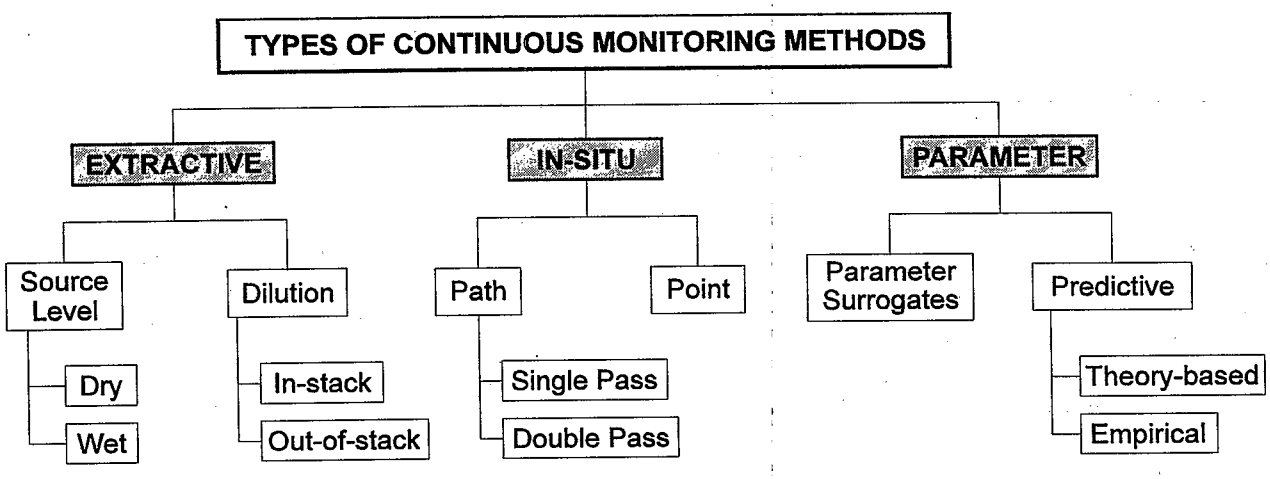

Figure 1-1. Continuous monitoring methods.

dioxide and oxygen. However, concentration measurements of metal vapors and complex organic compounds can be very difficult to perform in field installations. With the advent of modern microprocessor systems, sophisticated laboratory analytical techniques have become available for field use at relatively low cost. Fourier transform infrared spectroscopy (FTIR) and gas chromatographic mass spectroscopy (GCMS) are two such methods that can be used for measurement of a wide range of compounds. Other techniques, such as ion mobility spectroscopy, the use of diode lasers in optical differential absorption systems, and the advent of low-cost catalytic or semi-conductor sensors provide options for monitoring acid and organic gases that were previously very difficult and expensive to monitor on a continuous basis.

Technologies for the measurement of flue gas metal concentrations are developing. The partition of metals between the gas phase and particles provides a challenge in obtaining a representative sample and in making the actual measurement. Some metals, such as mercury, are relatively easy to monitor in the vapor state. When metals are bound in the particulate matter, the continuous measurement of particulate mass concentration can monitor an upper bound of metal emissions. Continuous particulate mass measurement techniques are well established, having evolved in Europe over the past 20 years (Peeler, 1996).

In some cases, sensors used to monitor plant or control equipment performance parameters also can provide continuous data for emissions tracking. Here, data obtained from the sensors are used in place of actually determining emission concentrations. A sensor-determined value is assumed to stand in place of, or correlate to, emissions levels expressed in ppm or mg/m^3. This approach has been used in NSPS requirements since 1975 and may see greater application for process units regulated under the proposed CAM rule. Rather than just serving as emissions surrogates, operational parameter data can also be incorporated into computer models to predict emissions. These models generally are developed by correlating parameter data to actual source test data obtained over a range of operating conditions. However, to develop a robust model, one that remains valid under a wide range of operating conditions, the costs associated with source testing may become comparable with the actual cost of CEM instrumentation.

One of the central problems associated with monitoring hazardous air pollutants is the lack of established or validated reference methods. Traditionally, CEM systems have been certified for use at a facility by performing a series of wet chemical or instrumental reference method tests. The tests are used to determine the "relative accuracy," the accuracy of the CEM system relative to the reference method values. In the past, the effect of other gases on the reference test method results was generally well understood for specific industrial processes. Collaborative tests and years of field data have given confidence that the reference methods indeed give true emission reference values under most conditions.

To similarly validate reference methods for the hazardous, non-criteria pollutants has been difficult.

The reactive nature of many of these gases, their presence in gaseous and solid forms, and their low concentration in flue gases, provide challenges for wet chemical reference methods and instrumental monitoring techniques alike. Because of these problems, few reference methods for the hazardous, non-criteria pollutants have been established. Instead, several new approaches using reference spectra, internal standards, and dynamic spiking offer alternative approval mechanisms.

The engineer choosing between the various monitoring options is of course, looking for the "best" system. However, no generic "best system" exists. CEM systems are application dependent; depending upon regulatory requirements, pollutants to be monitored, location restrictions, flue gas conditions, ambient conditions, and manpower and management considerations. Cost is a factor in choosing a system, but low cost should never be the single deciding factor. In the end, the best system will be one that can analyze a sample representative of flue gas conditions, one that meets all regulatory requirements for accuracy and precision, and one that has low capital costs and low maintenance requirements.

When choosing between parameter surrogates, predictive systems, or CEM systems, cost can be viewed from a different perspective. When applied to market trading programs, the value of an emissions "credit" or "allowance" may be related to how the credit is determined. Credits determined with some uncertainty may be worth less than those obtained with more certainty. In the end, the cost associated with the monitoring method may be counterbalanced by the consequent value of the data.

The decision-making process for choosing a CEM system can become very complex (White, 1995). All of the decision factors for the "best" system are, of course, relative. For example, a 10% relative accuracy may be important for a trading program; however, a 20% relative accuracy may be adequate if normal emissions are at a 50 ppm level when the emissions standard has been set at 200 ppm. Monitoring costs may not be a significant factor when facing $25,000/day penalties for noncompliance, but a small manufacturing facility may not have the capital or manpower necessary to maintain a complex electro-optical monitoring system. This Handbook has been prepared to provide information that can assist the decision-maker in choosing between the variety of available monitoring options.

1.4 Organization of the Handbook

The Handbook is organized in a manner that allows the reader to proceed from a logical progression from implementing rules, technical evaluation, system purchase, and certification. The objective of the Handbook is to provide the reader with the conceptual tools and detailed information necessary to make informed decisions with regard to the monitoring options available.

- The implementing rules through which CEM systems are required to be installed are addressed in Chapter 2. This chapter contains a discussion of various regulations and monitoring programs to assist in evaluating non-criteria pollutant monitoring programs in the context of established regulatory concepts. The chapter provides a review of existing requirements, emphasizing those where non-criteria pollutant monitoring is required.

- Current monitoring instrumentation is discussed in Chapter 3. The authors focus on the dependence of the sampling system and instrumentation on the pollutants to be measured. Reactive and condensable gases, particulate matter, and metals present specific challenges. Due to the special sampling requirements for non-criteria pollutants, sampling systems are addressed separately for gases and particulate matter. The analytical techniques used in analyzers designed for monitoring HAPs and particulate matter are presented.

- Non-traditional methods of monitoring source emissions, focusing on the parameter (surrogate) monitoring and predictive monitoring (modeling) methods, are addressed in Chapter 4. Advantages and disadvantages of the methods and the concept that the combination of CEM instrumentation with modeling methods makes for a powerful tool for both monitoring and process control are advanced in this chapter.

- An important subsystem associated with any monitoring program, the data acquisition and handling system, is discussed in Chapter 5. The state-of-the art of CEM system data acquisition, control, and reporting systems is reviewed in this chapter. It provides a review of the various options available and how they fit into the total system package.

- Common sense approaches to choosing a monitoring system, emphasizing the relationship of the type of CEM system or monitoring technique to the application, are discussed in Chapter 6. This chapter describes what information is needed prior to writing the technical specifications, how to write a technical specification, and how to evaluate bids received.

- Certification and approval mechanisms that can be used for validating non-criteria pollutant monitoring systems are addressed in Chapter 7. Mechanisms are necessary to provide assurances that the installed system will provide data that provide a degree of representativeness, accuracy, and precision consistent with regulatory specifications. Approval procedures specific to advanced monitoring techniques are presented. Issues involved with multi-component systems (such as FTIR and GCMS), where many compounds may be measured concurrently or sequentially, are discussed with respect to procedures that may be required for demonstrating system and analytical performance both on an initial and continuing basis.

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Chapter 2
Implementing Rules - Requirements for Installation of CEM Systems

A discussion of various regulations is presented in this chapter to help the user evaluate non-criteria pollutant monitoring programs in the context of established regulatory concepts. A review of current requirements, emphasizing those where non-criteria pollutant monitoring is required, is also presented. Monitoring regulations now being developed are discussed briefly.

The information contained in this chapter is intended for those that are new to the field of continuous monitoring. Understanding the evolution of existing monitoring requirements and the interrelationship of different regulatory programs is especially important in the development of new monitoring programs. The following sections illustrate a range of monitoring approaches, quality assurance requirements, and regulatory uses of continuous monitoring data. This background information will be helpful in establishing and negotiating monitoring requirements for non-criteria pollutant monitoring programs.

2.1 Clean Air Act, RCRA, and Other Federal Monitoring Requirements

Federal pollutant monitoring requirements for air emissions are contained in regulations developed under several different statutes. Most notably, monitoring requirements are included in several different regulatory programs developed over the last twenty-five years under the Clean Air Act (CAA). These have included new source performance standards, national emission standards for hazardous pollutants, and the acid rain program. Also under the Clean Air Act authority, the EPA has established federal requirements for states to adopt and implement pollutant monitoring programs in State Implementation Plans designed to achieve conformance with ambient air quality standards. These requirements are contained in Part 51.

Air pollutant emissions from sources that burn hazardous waste are regulated under federal regulations derived from the Resource Conservation and Recovery Act (RCRA). Proposed revisions to the hazardous waste combustor regulations combine the CAA air program requirements and RCRA requirements into a single set of regulations for these sources. Air pollutant emissions from sewage sludge incinerators are regulated under Section 503 of the Clean Water Act. Emissions of radioactive materials are not described here.

2.1.1 NSPS Requirements

EPA regulations contained in 40 CFR 60, "Standards of Performance for New Stationary Sources," (commonly referred to as NSPS) apply to selected categories of stationary sources of air pollution for which EPA has developed specific regulations to limit emissions of criteria pollutants and certain designated pollutants. Over the past 25 years, the EPA has developed NSPS regulations for more than 68 source categories. In most cases, these regulations only apply to sources above specific size thresholds and for which construction began after the date of the proposed regulation. NSPS regulations limit emissions of criteria air pollutants including particulate, SO_2, NO_x, and CO. Emissions of volatile organic compounds (VOCs) also are limited because of their role in photochemical reactions resulting in the formation of ozone in the ambient air. Other non-criteria pollutants that are regulated directly or indirectly under NSPS include total reduced sulfur compounds (TRS), hydrogen sulfide (H_2S), and hydrogen chloride (HCl).

NSPS regulations are designed to require the installation and proper operation of "best demonstrated control" better known as "Best Available Control Technology" (BACT) to minimize emissions of pollutants. In general, a performance-based approach has been adopted whereby an affected facility can choose any method of pollutant reduction provided that the source operator can demonstrate compliance with the applicable emission limits by conducting performance tests. In most cases, specific test methods or monitoring requirements for conducting the demonstration of compliance are detailed within the applicable NSPS regulations. Where possible, the same methods that were used during the standard setting process to

determine the level of pollutant emissions corresponding to BACT are also used to demonstrate compliance. In this way, the uncertainty (bias and imprecision) of the measurement method and the averaging period of the applicable standard are taken into account. Because of this approach, the exact test methods and monitoring procedures used for compliance demonstrations are of great importance. Test methods are found in Appendix A and Performance Specifications for continuous emission monitors are included in Appendix B of 40 CFR 60.

Many sources subject to NSPS particulate emission standards are also subject to an opacity standard. For the most part, compliance with the opacity standard is determined by a trained human observer in accordance with EPA Method 9. Continuous monitoring of opacity of emissions is required for certain sources. NSPS regulations adopted since the 1977 Clean Air Act Amendments have prescribed "percent removal" requirements in addition to emission limitations for certain sources. In some cases, continuous emissions monitoring is required to demonstrate compliance with percent removal requirements.

2.1.1.1 "Proper O&M Monitoring" versus "Compliance Monitoring"

Initial NSPS regulations required the use of specific manual test methods for demonstrating compliance with particulate, SO_2, and NO_x emission limits. Method 9, Visible Emission Observations, was specified for determining compliance with opacity standards. CEM requirements for large boilers (heat input ≥ 250 million BTU/hr), sulfuric and nitric acid plants, and non-ferrous smelters were included in NSPS regulations promulgated in December of 1971. The data provided by these monitors could not be used to determine compliance with emission limits but were used instead to determine if a source was "properly operating and maintaining process and control equipment in a manner consistent with good air pollution control practices" as is required by 60.11(d). This regulatory application of continuous monitors has become known as "proper O&M monitoring." Monitoring results have been used to enforce the requirement of 60.11(d). These monitoring results have also been used as a trigger for other activities such as agency source inspections, visible emission observations, or requiring additional compliance demonstration tests. The EPA expanded this regulatory application of a CEM system to other source categories in subsequent regulations. Today, opacity CEM systems are by far the most widely used monitoring technique at NSPS sources. They remain as tools for enforcement of the general 60.11(d) proper O&M monitoring requirement rather than for direct determination of compliance with applicable opacity standards.

Subsequent to the 1977 CAAA, NSPS Subpart Da was proposed and later promulgated after litigation. Subpart Da applies to large electric utility steam generators constructed after Sept. 1978. It requires the use of a CEM system for the continuous demonstration of compliance with SO_2 and NO_x emission standards and SO_2 percent removal requirements. Compliance with these requirements is determined on a thirty-day rolling average basis. Subpart Da requirements include explicit minimum data availability requirements and also impose additional quality assurance requirements for SO_2 and NO_x CEM systems contained in Appendix F, Procedure 1 of Part 60. Since the promulgation of Subpart Da, continuous compliance monitoring applications of SO_2 and NO_x CEM systems have been promulgated for other large boilers, municipal waste combustors, and several other source categories.

2.1.1.2 Summary of NSPS Criteria Pollutant Monitoring Requirements

A summary of the NSPS criteria pollutant continuous emission monitoring requirements is presented in Table 2-1. Diluent (O_2 or CO_2) monitoring that is required to convert pollutant concentrations to units of the applicable standard is also indicated for different source categories. The compliance averaging period for CEM data is shown for those source categories and pollutants where monitoring data are used to demonstrate compliance with emission standards. The time period for determining and reporting excess emissions is shown for other monitoring applications. The reader is cautioned that exemptions and exceptions affecting many sources are detailed within the regulations for some source categories. The actual Part 60 regulations should be consulted for additional information, specific exemptions, averaging periods, reporting requirements, and other information.

2.1.1.3 Summary of NSPS Non-criteria Pollutant Monitoring Requirements

A summary of the NSPS non-criteria pollutant monitoring requirements is presented in Table 2-2. Existing non-criteria pollutant monitoring requirements address emissions of volatile organic compounds (VOCs), total reduced sulfur compounds (TRS), and hydrogen sulfide (H_2S) monitoring in petroleum refinery fuel gas. All of the NSPS non-criteria pollutant monitoring applications are used to ensure proper operation and maintenance of source process and control equipment. Emissions exceeding specific

Table 2-1. NSPS Criteria Pollutant Monitoring Requirements

Subpart - Effective Date	Source Category and Type	Pollutant and Diluent Monitors	Compliance Averaging Period For CEMS DATA	Excess Emissions Reporting Period
D - 8/17/71	Fossil Fuel-Fired Steam Generators > 250 x 10^6 Btu/hour heat input	SO_2 and NO_x (O_2 or CO_2 as diluent)		3 hours
		Opacity		6 minutes
Da - 9/18/78	Electric Utility Steam Generating Units > 73 MW (250 x 10^6 Btu/hour) heat input	SO_2 and NO_x emissions, SO_2 percent removal (O_2 or CO_2 as diluent)	30-day rolling average (boiler operating days)	
		Opacity		6 minutes
Db - 11/25/86 NO_x 6/19/84	Industrial-Commercial-Institutional Steam Generators >29 MW (100 x 10^6 Btu/hour) heat input	SO_2 and NO_x emissions, SO_2 percent removal (O_2 or CO_2 as diluent)	30-day rolling average (boiler operating days)	
		Opacity		6 minutes
Dc - 6/9/89	Small Industrial-Commercial-Institutional Steam Generators >2.9 MW < 29 MW (10 to 100 x 10^6 Btu/hour) heat input	SO_2 emissions, SO_2 percent removal (certain sources) (O_2 or CO_2 as diluent)	30-day rolling average (boiler operating days)	
		Opacity		6 minutes
Ea - 12/20/89	Municipal Waste Combustors >250 tons/day	SO_2 with O_2 as diluent, SO_2 percent removal (certain sources)	24 hours	
		NO_x emissions with O_2 as diluent	24 hours	
		CO with O_2 as diluent	4 hour and 24 hour periods	
		Opacity		6 minutes
F - 8/17/71	Portland Cement Plants	Opacity		6 minutes
G - 8/17/71	Nitric Acid Plants	NO_x emissions		3 hours
H - 8/17/71	Sulfuric Acid Plants	SO_2 emissions (O_2 or CO_2 monitors or other procedures to calculate emissions)		3 hours
J - 6/11/73	Petroleum Refineries			
	Fluid Catalytic Cracking Unit Regenerators	CO		1-hour
		SO_2 emissions SO_2 removal, sulfur oxides (certain sources)	7-day rolling average	
		Opacity		6 minutes
J - 6/11/73	Fuel Gas Combustion Devices	SO_2 with O_2 as diluent, (H_2S in fuel gas as alternative)		3-hour rolling average

Table 2-1. Continued.

Subpart - Effective Date	Source Category and Type	Pollutant and Diluent Monitors	Compliance Averaging Period For CEMS DATA	Excess Emissions Reporting Period
J - 10/4/76	Claus Sulfur recovery Plant > 20 LTD* with oxidation control system	SO_2 with O_2 as diluent		12 hours
J - 10/4/76	Claus Sulfur recovery Plant > 20 LTD with reduction control system	TRS with O_2 as diluent or dilution sampling system with oxidation and SO_2 with O_2 as diluent		12 hours
P - 10/16/74	Primary Copper Smelter			
	Dryer	Opacity		6 minutes
	Roaster, smelting furnace, and copper converter	SO_2	6-hour period	
R - 10/16/74	Primary Lead Smelter			
	Blast furnace, dross reverberatory furnace, or sintering machine discharge	Opacity		6 minutes
	Sintering machine, electric smelting furnace, and converter	SO_2	2-hour period	
Z - 10/21/74	Ferroalloy Product Facilities, submerged electric arc furnaces	Opacity		6 minutes
AA - 10/21/74 to 8/17/83	Steel Plants-Electric Arc Furnaces and Argon Decarburization Vessels (exceptions for certain controls)	Opacity		6 minutes
Aaa - 8/17/83	Steel Plants - Electric Arc Furnaces and Argon Decarburization vessels (exceptions for certain controls)	Opacity		6 minutes
BB - 9/24/76	Kraft Pulp Mills			
	Recovery Furnaces	Opacity		6 minutes
CC - 6/15/79	Glass Manufacturing Plants	Opacity		6 minutes
HH - 5/3/77	Lime Manufacturing Plants, rotary lime kilns	Opacity		6 minutes
NN - 9/21/79	Phosphate Rock Plants, dryers, calciners, and grinders	Opacity		6 minutes
LLL - 1/20/84	Onshore Natural Gas Processing, sweetening units	Velocity (also SO_2 if oxidation control system or reduction control system followed by incinerator is used)		24 hours
UUU - 4/23/86	Calciners and Dryers in Mineral Industries (with dry control devices)	Opacity		6 minutes

*LTD = Long Tons per Day

Table 2-2. NSPS Non-criteria Pollutant Monitoring Requirements

Subpart - Effective Date	Source Category and Type	Pollutant and Diluent Monitors	Excess Emissions Reporting Period
J	Petroleum Refineries		
J - 6/11/73	Fuel Gas Combustion Devices	H_2S in fuel gas (as alternative to SO_2 with O_2 in emissions)	3-hour rolling average
J - 10/4/76	Claus Sulfur recovery Plant > 20 LTD with reduction control system	TRS with O_2 as diluent or dilution sampling system with oxidation and SO_2 with O_2 as diluent	12 hours
BB - 9/24/76	Kraft Pulp Mills - Emissions from recovery boilers, lime kilns, digester system, brown stock washer system, evaporator, and condensate stripper systems	TRS with O_2 as diluent	12 hours
DDD - 9/30/87	VOC Emissions from Polymer Industry		
	Carbon absorbers	VOC	3 hours
	Condensers	Temperature or VOC	3 hours
FFF - 1/18/83	Flexible Vinyl and Urethane Coating and Printing - Rotogravure printing lines with recovery units	VOC	3 hours
III - 10/21/83	Synthetic Organic Chemical Manufacturing Industry - Units with air oxidation reactors	Specified parameters or VOC CEMS	3 hours
LLL - 1/20/84	Onshore Natural Gas Processing, sweetening units	velocity, (TRS and/or SO_2 as alternative for certain sources)	24 hours
QQQ - 5/4/87	Petroleum Refinery Waste Water System - Units with carbon absorbers	VOC	3 hours
SSS - 1/22/86	Magnetic Tape Coating Facilities - Units with carbon absorbers	VOC inlet and outlet streams for certain sources	3 hours
VVV - 4/30/87	Polymeric Coating of Supporting Substrates - Units with carbon absorbers	VOC inlet and outlet streams for certain sources	3 hours

levels are reported as "excess emissions." The monitoring results from these applications are not used to determine compliance with emission standards. Other designated pollutants such as HCl are regulated in Part 60 because of potential welfare impacts resulting from emissions. During the development of the Subpart Ea for municipal waste combustors, the EPA considered including an HCl continuous emission monitoring requirement. However, the final rule relies on annual HCl emissions tests in conjunction with the continuous demonstration of SO_2 removal efficiency to control HCl emissions. In this case, the continuous monitoring of SO_2 emission levels upstream and downstream of the acid gas control device serves as a surrogate for the direct monitoring of HCl emissions.

2.1.1.4 NSPS Parameter Monitoring Requirements

Many parameter monitoring requirements are included in NSPS regulations with measurement frequencies ranging from monthly to continuous. Selected NSPS parameter monitoring requirements are presented in Table 2-3. Similar requirements are contained in the applicable regulations for many other source categories. These and other NSPS parameter monitoring requirements are necessary for a variety of purposes.

Table 2-3. Example NSPS Parameter Monitoring Requirements

Subpart	Source Category and Type	Parameter	Measurement Frequency	Accuracy
O	Sewage Treatment Plants	feed rate	continuously	±5%
		fuel flow rate to incinerator	continuously	±5%
E,F,G,S	Incinerators, Portland Cement Plants, Nitric Acid Plants, Primary Aluminum Reduction Plants	feed rate or production rate	daily	±2%
GG	Stationary Gas Turbines	natural gas flow rate	continuously	±5%
		water to fuel ratio	continuously	±5%
DDD,III,NNN	VOC Emissions from; Polymer Manufacturing Industry, SOCMI Air Oxidation Unit Processes, and SOCMI Distillation Operations	absorber scrubber liquid temperature and specific gravity	continuously	±1% or ±0.5°C and ±0.02 s.g
		boiler or process heater combustion temperature	continuously or every 15 minutes	±1% or ±0.5°C
		flare (on/off)	continuously	
		incinerator combustion temperature	continuously	±1% or ±0.5°C
N,O,Y,HH, LL and many others	Secondary Emissions from Basic Oxygen Steelmaking Facilities, Sewage Treatment Plants, Coal Preparation Plants, Lime Manufacturing Plants, Metallic Mineral Processing Plants	wet scrubber pressure drop	continuously	±1 inch H_2O

Parameter monitoring may be required where pollutant monitoring is impractical or infeasible. For example, NSPS regulations provide an exemption from continuous opacity monitoring requirements if condensed water (droplets) exist at the monitoring location and interfere with the measurement. Monitoring certain parameters is required for determining process or production rates in conjunction with pollutant monitoring data to determine emissions in units of the standard. For example, sulfuric and nitric acid plants monitor certain process parameters to calculate the mass of SO_2 or NO_x emitted per ton of acid produced. Steam generators that combust varying fuel mixtures must monitor the heat input rate (fuel usage) for each fuel to select appropriate F-factors and properly calculate emissions in units of mass of pollutant per unit of heat input. Other sources are required to monitor production rate or operating hours to demonstrate that they are exempt from a particular monitoring requirement.

A number of "demonstrated compliance parameter level" approaches occur within NSPS regulations. In these applications, a specific parameter level is prescribed within the regulation or determined by empirical tests that will ensure compliance with the emission limitation. Thus, the parameter value becomes a surrogate for the emission limit. For example, the outlet temperature for catalytic VOC incinerators must be monitored and maintained above a minimum to ensure that VOCs are combusted properly. As another example, the water injection rates necessary to achieve compliance with NO_x emission limits for an NSPS Subpart GG gas turbine are demonstrated at each of four operating loads during the initial compliance test. Subsequently, the operating load and water injection rate are monitored continuously to ensure compliance with NO_x emission limitations.

Other NSPS parameter monitoring requirements are quite diverse. They include monitoring of sulfur content of coal to calculate SO_2 emissions for certain sources where SO_2 monitoring is not required and for other sources where fuel sulfur pretreatment credits are applied towards SO_2 removal requirements. Certain source categories involved in coating operations must monitor the VOC content of coatings to demonstrate compliance with applicable limits. Other sources must monitor compliance with various "work practice standards" ranging from simply covering solvent containers or closing ventilation

hood inspection doors, to wetting of unpaved roads to reduce fugitive particulate emissions at stone and mineral processing facilities. These types of requirements are specific to particular source categories. They are established during the rule making process in consideration of many factors including technology limitations and cost.

2.1.1.5 NSPS Monitoring Regulations and Performance Specifications

Important aspects of NSPS CEM programs are prescribed in several sections of 40 CFR 60. Requirements applicable to all sources are found in "Subpart A. General Provisions." Of these, "§60.13 Monitoring Requirements" includes requirements for source operators to conduct daily zero and upscale calibration checks, to perform an initial test of each CEM system in accordance with applicable Appendix B Performance Specifications, and other essential elements of a monitoring program. Other requirements applicable to continuous monitoring programs are found in §60.7 Notification and Recordkeeping, and §60.11 Compliance with Standards and Maintenance Requirements.

Generally, each source category subpart with a continuous monitoring requirement includes (or references) additional specific monitoring requirements and information. This typically includes requirements for the selection of the monitor span value, identification of Appendix A test methods that may be used to conduct relative accuracy tests, methods for converting emissions to units of the standard, and other technical requirements. For proper O&M monitoring applications, reporting requirements and specifications used to identify periods of excess emissions are included. For compliance monitoring applications, emissions averaging periods and detailed compliance reporting requirements are included.

Appendix B of Part 60 includes CEM performance specifications for a number of different compounds and applications. These are listed in Table 2-4. These specifications and procedures are used to determine whether a particular CEM system is acceptable at the time of, or soon after, installation at a particular source. The performance specifications are the minimum procedures that are required to determine if a CEM system is capable of providing reliable measurements. They are not sufficient to assure the quality of the data obtained on an ongoing basis. The first three specifications were originally promulgated in October 1975 and have been revised substantially several times.

Performance Specification 1 (PS 1) applies to opacity monitors and includes a detailed list of <u>design specifications</u> to prescribe how the optical transmission measurement is to be made. In addition, <u>performance specifications</u> are included in PS 1 to determine 1) the stability of the monitor response relative to its simulated zero and upscale calibration checks, 2) the monitor's calibration error relative to a set of external optical density filters, and 3) the instrument's capability to operate for a period of two weeks without unscheduled maintenance or repairs. PS 1 does not include a relative accuracy specification because no independent method is available to measure the in-stack opacity. (Substantial technical and administrative revisions to PS 1 were proposed on November 25, 1994 (59 FR 60585). EPA's and industry's consideration of these revisions is ongoing at the time of this writing.)

All other performance specifications reflect a different approach than PS 1. No substantial design requirements are included. In essence, any sampling system configuration and/or any analytical approach may be used provided that the measurement system can be shown to meet two basic performance specifications. First, a drift test is conducted over a one-week period to evaluate the stability of the monitor response relative to the calibration materials and the procedure used for the daily zero and upscale calibration checks. Second, a relative accuracy test is performed that involves the comparison of the CEM system measurement results with concurrent independent pollutant measurements obtained through the use of specified test methods found in Appendix A of Part 60. The relative accuracy test includes a minimum of nine runs although twelve are more common since the tester is free to reject up to three runs on an arbitrary basis. The computation of the relative accuracy test result includes both mean difference and confidence coefficient terms based on the paired CEM system and reference test results. Thus, both the accuracy and precision of the paired measurements are evaluated. Failure of a relative accuracy test may be due to problems with the CEM system, problems with the reference test methods, problems with the representativeness of the sampling location, or other factors. A failed test requires careful investigation to determine the cause and then it must be repeated. A successful relative accuracy test is considered to be an adequate demonstration of the monitor's <u>capability</u> to provide reliable data.

Table 2-4. NSPS Appendix B Performance Specifications

Performance Specifications	CEM Systems
PS 1	Opacity
PS 2	SO_2 and NO_x
PS 3	O_2 and CO_2
PS 4	CO
PS 4A	CO (applicable for municipal waste combustors)
PS 5	TRS
PS 6	Continuous Flow
PS 7	H_2S (H_2S in fuel gas)
PS 8	VOC
PS 9	Gas Chromatography

Performance Specifications 2 (SO_2 and NO_x) and 3 (O_2 and CO_2) were promulgated originally in October of 1975 and included relative accuracy, calibration error, response time, 2- and 24-hour zero and calibration drift specifications, and continuous operational requirements for two separate one-week periods. Numerous corrections and more detailed technical test procedures were proposed as revisions to PS 2 and 3 during 1983 in response to severe industry criticism of the existing performance specifications. (This criticism arose as a result of the proposal, and subsequent promulgation, of Subpart Da which included the first use of a CEM system for compliance monitoring.) The 1983 proposed revisions to PS 2 were met with more objections from the utility industry. The EPA subsequently reproposed and then promulgated revisions to PS 2 which eliminated all of the performance specifications except for relative accuracy and the seven-week drift test. In addition, specific CEM measurement location requirements were reduced with general guidance. These changes reduced the prescriptiveness of the regulations and placed the responsibility on industry for determining the acceptability of monitoring systems. This philosophy has been maintained in revisions to PS 2 and 3 and has been used to develop PS 4 through PS 8. A different approach has been used for PS 9 which eliminates the relative accuracy test and relies solely on the use of a multiple calibration gases to assess the accuracy of the monitoring data.

Appendix F, Procedure 1 of Part 60 prescribes quality assurance requirements for CEM systems that are used to demonstrate compliance with emission limitations or percent removal requirements. They include: 1) requirements to develop quality control procedures for five specific activities, 2) "out-of-control" limits on daily zero and calibration drift check results for determining when data can not be used to satisfy minimum data requirements, and 3) quarterly accuracy assessment procedures and "out-of-control" criteria for such audits. Procedure 1 requires that a relative accuracy audit be performed each year as one of the quarterly accuracy audits. Three-run relative accuracy audits or cylinder gas audits may be performed for the other three quarters.

2.1.2 Acid Rain Program

EPA has developed the Acid Rain Program in response to the 1990 Clean Air Act Amendments. The program seeks to reduce SO_2 emissions from the electric utility industry by 10 million tons per year (relative to 1985 emissions) by the year 2010 utilizing a market-based trading approach. Under this program, each electric utility generating unit received the right to emit a certain quantity of SO_2 each year. This right is expressed as a number of "allowances" to emit one ton of SO_2. An allowance trading program has been established to provide for the sale or exchange of SO_2 allowances between electric utility units, companies, or other parties. Market forces within the utility industry are expected to determine the most effective means of

achieving the overall SO_2 emission reduction. Additional regulations are being developed to limit emissions of NO_x from the utility industry as part of the Acid Rain Program.

Extensive continuous emission monitoring programs serve as the basis for the allowance trading program. These monitoring regulations are contained in 40 CFR 75 and require continuous monitoring of SO_2 and stack gas flow rate to determine the mass emission rate of SO_2 (i.e., lb. SO_2 per hour, tons SO_2 per year). Monitoring of NO_x and diluent (O_2 or CO_2) concentrations also is required to determine emissions in units of lb. NO_x per million Btu of heat input. (These sources must also report mass emissions of CO_2.) The allowance trading program is based on the premise that all emissions must be accounted for. Thus, great emphasis has been placed on the accuracy of the monitoring data at all operating conditions (rather than only at the emission standard level) in the adoption of Part 75 performance specifications and quality assurance procedures. In addition, special procedures have been developed to account for missing data. Within the data substitution procedures required for missing data, incentives are provided for affected sources to achieve high levels of CEM availability. Other key aspects of the Acid Rain Program are the development of electronic reporting mechanisms and comprehensive efforts to implement the program on a consistent basis in all states and jurisdictions.

Essentially, the largest 263 SO_2 emission sources were identified within the 1990 CAAA as Phase 1 sources. All other affected utility sources (approximately 2,000 units) are designated as Phase 2 units. Phase 1 units were required to have a CEM system installed and certified before November 1994. All Phase 2 units were required to have a CEM system installed and certified by Dec. 31, 1995 with the exception of certain gas-fired units and peaking units. The vast majority of all of the affected units were able to install and certify the required CEM system by the applicable deadlines (EPA, 1995a).

2.1.2.1 Flow Rate Monitoring

Before the development of the Acid Rain program, there was little experience with stack gas flow rate monitors installed as part of emission monitoring systems. The performance and reliability of these devices was a very controversial subject during the development of the Part 75 regulations. However, experience has shown that flow rate monitors are capable of meeting the applicable performance specifications in Appendix A of Part 75 including the relative accuracy tests conducted at three different operating loads (Bensink, 1995). Stack gas flow rate monitors are considered reliable monitoring devices even though differences between the stack gas volumetric flow rate determined by heat rate calculations and by flow rate monitors continue to be the subject of investigation by both the EPA and the utility industry.

2.1.2.2 Part 75 Performance Specifications and QA Requirements

These requirements are similar, though somewhat more restrictive, than the Part 60 requirements. The Part 75 performance specifications require use of calibration gases to check the performance of all gas monitoring systems. The specifications include response time tests and a three-point calibration error test. A bias test is also included that is based on comparison of the mean difference and confidence coefficient terms determined during the relative accuracy test. The regulations require application of a bias adjustment factor to emission values if the CEM data are biased low by an amount greater than the confidence coefficient relative to the reference method data.

Part 75 Appendix B quality assurance requirements are also similar to Part 60 requirements. Accuracy audits are required twice each year except for those units which achieve an "incentive" specification in the relative accuracy test. Units that achieve a relative accuracy of less than 7.5% are allowed to perform a single accuracy audit each year.

2.1.3 NESHAP and Title III - MACT Standards

2.1.3.1 Part 61 Existing NESHAP

National emission standards for hazardous air pollutants (NESHAP) are contained in 40 CFR 61. Prior to 1992, EPA promulgated NESHAP for 22 source categories. These regulations limit emissions of arsenic, asbestos, benzene, beryllium, mercury, vinyl chloride, radon, radionuclides, and HAP fugitive emissions from equipment leaks.

Several of the NESHAP regulations include CEM requirements. Subpart A General Provisions, §61.14 includes general monitoring requirements for sources required to monitor continuously. Opacity monitors are required for sources affected by Subparts N, O, and P regulating inorganic arsenic emissions from glass manufacturing plants, copper smelters, and from arsenic trioxide and metal arsenic production plants, respectively. These regulations refer to Performance Specification 1 in Part 60 for evaluations of opacity CEM systems. In addition, parameter monitoring requirements similar to those contained in Part 60 are included for certain sources. Subpart

F requires installation of vinyl chloride CEM systems at certain emission points in ethylene dichloride, vinyl chloride, and polyvinyl chloride plants. Subpart F, §61.68 includes specific technical requirements for monitoring systems that use gas chromatography and flame ionization detectors for analysis of sequential samples. Daily span checks with a 10 ppm calibration gas are required. Procedures contained in Appendix B, Method 106 are referenced for certification of vinyl chloride cylinder standards and for the preparation of calibration curves. A summary of NESHAP monitoring requirements is included in the "Enhanced Monitoring Reference Document" (EPA, 1993).

2.1.3.2 MACT Standards

Title III, Section 112 of the 1990 CAAA identified a list of 189 hazardous air pollutants (HAPs) and requires EPA to establish new NESHAPs for all major sources of HAPs (Appendix A) in accordance with a prescribed regulatory schedule. Major sources are defined as those that emit more than 10 tons per year of one HAP or more than 25 tons per year of a combination of HAPs. The schedule for promulgation of these new standards for affected source categories was originally published in the July 16, 1992 Federal Register (57 FR 31576). The schedule organized sources into "bins." The two-year bin included 40 source categories for which standards were to be promulgated by November 1992. The four-year bin included 25 percent of the listed source categories and the seven-year bin included 50 percent of the listed source categories. All listed categories are to have standards set no later than November 2000.

These regulations are being developed for inclusion in 40 CFR 63 and specify the maximum achievable control technology (MACT) for each source category. The CAAA require sources to obtain case-by-case MACT determinations if EPA has not promulgated a standard within 18 months of the scheduled date.

The MACT standards will include monitoring provisions that will satisfy the requirements of the Act to ensure that source owners are able to certify as to the compliance status of affected emission units. These monitoring requirements will be at least as rigorous (i.e., direct emissions measurement and monitoring of enforceable operational limits) as requirements outlined under Part 64 or Part 70 periodic monitoring requirements. EPA has developed general provisions that are applicable to all MACT standards. The Part 63 General Provisions were promulgated March 16, 1994 and include performance testing, monitoring, and recordkeeping and reporting procedures for sources subject to MACT standards. A current listing of the MACT standards status is published periodically in the Federal Register by the EPA in accordance with the requirements of the CAA. (See April 17, 1996 notice on the EPA Technology Transfer Network (TTN) bulletin board, telephone no. 919-541-5742). Many of the MACT standards require inspection or monitoring of process or control device parameters on a quarterly, monthly, weekly, or daily basis. These requirements are not addressed in this handbook because of the frequency of the measurements. Few of the MACT standards include continuous monitoring requirements.

2.1.3.2.1 HON Rule - Example MACT Standard. As an example, the Hazardous Organic NESHAP (known as the "HON rule") covers manufacturing processes in the synthetic organic chemical manufacturing industry (SOCMI) and regulates emissions from about 370 facilities including approximately 111 of the 189 HAPS (EPA, 1994a). Subpart G of the HON rule contains regulations for emission points at SOCMI sources. Continuous monitoring requirements are summarized in Table 2-5.

2.1.3.2.2 Magnetic Tape - Example MACT Standard. Subpart EE of Part 63 applies to the production of magnetic tapes. Monitoring requirements similar to the HON rule apply for sources using combustion devices for control of volatile emissions. Those source using carbon adsorbers are required to install a CEM system for volatile organic hazardous emissions. Depending on the type of facility, either a total hydrocarbon monitor or a gas chromatograph with an appropriate detector can be used. Performance Specifications 8 and 9 in Appendix A of Part 60 are used to evaluate the performance of these types of CEM systems, respectively. Very similar requirements are found in NSPS Subpart SSS except that the requirements are intended for the control of VOCs.

2.1.3.2.3 Secondary Lead Smelters - Example MACT Standard. A final NESHAP (Part 63, Subpart X) for new and existing secondary lead smelters was published on June 23, 1995 (60 FR 32587). These facilities recover lead metal from scrap lead, primarily from used lead-acid automotive batteries and have been identified as significant emitters of lead and arsenic compounds, and 1,3-butadiene.

Table 2-5. HON Rule Example Continuous Monitoring Requirements

Emission Source	Control System	Monitoring	Frequency
Process Vents	thermal incinerator catalytic incinerator boiler or process heater flare scrubber bypass lines	firebox temp. inlet and outlet temp. firebox temp. presence of flame pH of effluent streams vent stream flow	continuous continuous continuous continuous continuous continuous
Storage Vessels	fixed roof external floating roof closed vent and control	visual inspection visual inspection presence of flame or flare	annual when filled continuous

The MACT standard regulates emissions of lead compounds as surrogates for all metal HAPs and total hydrocarbons (THC) as surrogates for all organic HAPs, respectively. Continuous monitoring requirements are included for baghouse operation and THC emissions.

The proposed regulation would have required the installation of a continuous opacity monitor and the development of a site-specific opacity standard to ensure adequate collection of metal HAPs. However, in view of the many comments opposed to this approach for technical and administrative reasons, the EPA modified this regulation. The final rules in §63.548, require a "standard operating procedure" (SOP) for baghouse inspection and maintenance, and a bag leak detection system with an alarm, and a corrective action procedure for responding to alarms. The bag leak detection system: 1) must be capable of detecting particulate matter concentrations at 1.0 mg/m^3, 2) must provide an output of relative or absolute particulate emissions, 3) must include an alarm system that activates upon detection of an increase in particulate emissions, 4) must be installed downstream of any wet acid gas scrubber or on each compartment of a positive pressure baghouse, and 5) must be installed and operated in a manner consistent with <u>any</u> available guidance from the EPA.

The secondary lead THC monitoring requirements apply to emissions from process sources (i.e., blast and reverberatory furnaces). The THC monitor is used to continuously monitor compliance (3-hour average) with the applicable emission limit ranging from 20 to 360 ppm (as propane) depending on the type of furnace used. The THC monitor must comply with the all of the CEM requirements in the Subpart A, General Provisions.

2.1.4 Regulations for Sources Burning Hazardous Waste

2.1.4.1 Existing Regulations for Sources Burning Hazardous Waste

2.1.4.1.1 Hazardous Waste Incinerators. The treatment of hazardous waste is regulated under the Resource Conservation and Recovery Act (RCRA). Hazardous waste is defined in Part 264. Air pollution emissions from hazardous waste incinerators are regulated in Part 265. Facilities subject to these regulations must demonstrate compliance with prescribed destruction and removal efficiencies (DREs) for metals and organic emissions. The DREs are determined during the Part B permit trial burn by comparing the quantity of materials fed into the incinerator with measured emission rates. Trial burns are extensive testing programs typically involving the measurement of emissions of speciated dioxin/furans, volatile organic compounds, non-dioxin/furan semi-volatile organic compounds, particulate, metals, HCl/Cl_2 and other components. Because of the extreme public concern regarding these facilities, source-specific trial burn plans are developed and negotiated with federal, state, and local agency representatives. Trial burn test results are subject to control agency and public review and are the basis for many of the requirements included in the incinerator operating permit. CEM requirements for CO and THC as well as incinerator and control device operation also are included in hazardous waste incinerator operating permits.

2.1.4.1.2 BIF Regulations. On February 21, 1991 (56 FR 7134), the EPA published a final rule controlling hazardous waste burning by boilers and industrial furnaces (known as the BIF Rule). Currently, the BIF Rule regulates emissions of HCl/Cl_2, CO, particulate matter, metals and organics in essentially the same manner as RCRA hazardous waste incinerators. BIF sources also are regulated under RCRA Standards for treatment, storage, and disposal of

hazardous waste. The BIF Rule organizes sources using a three-tiered approach for each target pollutant. Current provisions under the BIF Rule mandate continuous emission monitoring for CO, O_2, and hydrocarbons based on this approach (EPA, 1992).

Tier I of the BIF Rule limits CO emissions to 100 ppmv (dry) based on an hourly rolling average corrected to 7% O_2. Monitoring hydrocarbon emissions is not required if the source can meet this criteria. If the source cannot meet this 100 ppmv Tier I CO limit, then hydrocarbon monitoring is required in addition to CO and O_2 monitoring. The source is also regulated under Tier II controls. Under Tier II, hydrocarbon emissions are limited to 20 ppmv (dry, corrected to 7% O_2) and CO emissions are limited based upon levels demonstrated during the compliance test. Concentrations of CO and hydrocarbons must be continuously monitored and corrected to 7% O_2 on a dry basis. CEM systems for CO and hydrocarbons must complete a minimum of one cycle of sampling and analysis every 15 seconds, and must record one data point each successive minute. The 60 most recent 1-minute averages must be used to calculate the hourly rolling average.

The current performance specifications for CEM systems at BIF sources are included in 40 CFR, Part 266, Appendix IX, Section 2. Section 2.1 outlines the performance specifications for CO and O_2 analyzers. Included are procedures for conducting calibration drift, relative accuracy, calibration error, and response time tests to assess the conformance of the CEM system with the specifications. The reference methods used for the relative accuracy determinations are Methods 3 or 3A (for O_2), and Methods 10, 10A, or 10B (for CO) in 40 CFR 60, Appendix A. Performance specifications for hydrocarbon analyzers are found in Section 2.2 of the BIF Rule. They specify the use of a heated flame ionization analyzer and sampling system maintained between 150-175°C, and include procedures for conducting calibration error, calibration drift, and response time tests. (Provisions are included also for the interim use of sample conditioning systems that cool and dry the stack gas sample prior to the analyzer.) Relative accuracy test requirements are not included in Section 2.2. Instead, procedures to challenge the analyzer and system with calibration gases are used to determine the conformance of the CEM system with the specifications.

2.1.4.2 Revised Standards For Hazardous Waste Combustors

Proposed revisions were published in the Federal Register on April 19, 1996 to 40 CFR Parts 60, 63, 260, 261, 263, 266, 270, and 271 with respect to the regulations for sources burning hazardous waste (61 FR 17358). The rule was proposed under the joint authority of the CAA and RCRA. The proposed rulemaking action was taken for two main reasons; 1) to meet scheduled MACT standards requirements, and 2) because of settlement requirements of a lawsuit between the agency and several other parties. The proposed rule revises standards for hazardous waste combustors, boilers and industrial furnaces, and lightweight aggregate kilns burning hazardous waste as supplemental fuels. MACT standards are proposed for dioxin/furans, mercury, semivolatile metals (Cd, Pb), low volatile metals (Sb, As, Be, Cr), particulate matter, HCl, Cl_2, hydrocarbons, and CO.

The proposed rules reflect a multifaceted approach that establishes emission limits for dioxin/furans on a "toxic equivalent basis", uses hydrocarbons and CO as surrogates for volatile organic HAPs, and uses particulate matter as a surrogate for 1) non-dioxin/furin semi-volatile organics and 2) both low and semi-volatile metals. No surrogates are proposed for mercury and HCl/Cl_2. The proposed rule contains monitoring requirements for CO and O_2 (all data must be corrected to 7% O_2), hydrocarbons, particulate matter, and mercury. Continuous monitoring of HCl/Cl_2 and other metals is optional.

New performance specifications to be included in Part 60 have been proposed as follows:

PS 4B for CO and O_2 for incinerators, boilers, and industrial furnaces burning hazardous waste (previously published in 56 FR 32688 July 17, 1991, with BIF regulations, but not previously designated as PS 4B.)

PS 8A for hydrocarbons THC for incinerators, boilers, and industrial furnaces burning hazardous waste (previously published in 56 FR 32688 July 17, 1991, with BIF regulations, but not previously designated as PS 8A.)

PS 10A mercury, semivolatile metals, and low volatile metals for incinerators, boilers, and industrial furnaces burning hazardous waste (new).

PS 11A continuous monitoring of particulate matter for incinerators, boilers, and industrial furnaces burning hazardous waste (new but similar to ISO 10155).

PS 12A mercury emissions for incinerators, boilers, and industrial furnaces burning hazardous waste (new).

PS 13A HCl emissions for incinerators, boilers, and industrial furnaces burning hazardous waste (new).

PS 14A Cl_2 emissions for incinerators, boilers, and industrial furnaces burning hazardous waste (new).

Extensive discussions of EPA's determinations regarding the feasibility, availability, and performance of continuous monitors for organic compounds, metals, and particulate matter are included in the Technical Support Document 4A accompanying the proposed regulations. Many references to the experience with monitoring particulate and other components in Germany and Europe are included in the technical support documents and the preamble of the proposed regulations. EPA is conducting additional field evaluations for particulate and Hg monitors as the rulemaking proceeds.

2.1.5 Part 503 Sewage Sludge Incinerators

EPA promulgated CEM requirements for sewage sludge incinerators on February 19, 1993 in 40 CFR 503 under authority of the Clean Water Act. Subpart E of that regulation, §503.45, requires the installation of a total hydrocarbon (THC) monitor and an oxygen monitor on each incinerator. The THC monitor must use a sampling system maintained at a temperature above 150°C and a flame ionization detector. Monitoring results are corrected to 7% O_2, dry basis, and affected sources are required to comply with an emission limit of 100 ppm. Detailed guidance with respect to these regulations is found in "THC Continuous Emission Monitoring Guidance for Part 503 Sewage Sludge Incinerators" (EPA, 1994b). Performance specifications and quality assurance procedures are modified from those in Part 60. No relative accuracy test involving independent THC measurements is required. Instead, these regulations rely on the use of calibration gases to assess the performance of the measurement system.

In response to certain petitioners, EPA published a modification to the sewage sludge incinerator monitoring requirements on February 25, 1994 (FR 9097). In this action, EPA agreed that a 100 ppm CO standard imposed by the state of New Jersey was more restrictive than the 100 ppm THC standard. EPA's amendment removed the THC requirement for those sources that install a CO monitor and can demonstrate continuous compliance with a 100 ppm CO standard (monthly average).

2.2 State and Local Agency Programs

Most state and local air pollution control agencies have broad authority to specify emission monitoring and test methods. Monitoring requirements may be adopted through applicable rulemaking procedures for certain source categories or they may be included in operating permits for individual sources on a case-by-case basis. Source-specific monitoring requirements are included in compliance orders or consent decrees as a result of enforcement activities.

On October 6, 1975 (FR 40 46247), EPA established requirements for states to adopt and implement continuous emission monitoring programs in state implementation plans designed to achieve conformance with ambient air quality standards. These requirements are contained in Appendix P to Part 51 - "Minimum Emission Monitoring Requirements." These minimum requirements identify affected source categories; prescribe monitoring, recording and reporting procedures for those sources; and detail performance specifications and procedures for converting monitoring data to units of the state emission standard. Appendix P states,

> "Such data must be reported to the State as an indication of whether proper maintenance and operating procedures are being utilized by source operators to maintain emission levels at or below emission standards. Such data may be used directly or indirectly for compliance determination or any other purpose deemed appropriate by the State."

Appendix P addresses: opacity, SO_2 and NO_x monitors (and diluent oxygen or carbon dioxide monitors) for certain fossil fuel-fired steam generators, opacity CEM systems for fluid bed catalytic cracking unit regenerators, SO_2 monitors for sulfuric acid plants, and NO_x monitors for nitric acid plants.

The minimum requirements included in Appendix P apply to opacity and criteria pollutant monitors at fossil fuel-fired steam generators, sulfuric acid plants, and nitric acid plants. Some states and local agencies have required CEM systems for additional sources and additional pollutants. In many cases, these regulations are similar to the requirements outlined in Appendix P.

2.2.1 State and Regional Initiatives

State and local air pollution control agencies have included continuous emission monitoring requirements in regulations and in permits for specific facilities. With respect to non-criteria pollutant monitors, many of these requirements are on a case-by-case basis. The following are some examples. New Jersey, Virginia, and Rhode Island have required installation of ammonia monitors at certain cogeneration or combined cycle turbine installations where NO_x control is required. A municipal waste combustor facility in Connecticut is conducting an evaluation of an installed HCl monitor to demonstrate that SO_2 removal efficiency across a spray dryer is an adequate surrogate for HCl emissions; the state agency is determining the viability of HCl monitors based on the same study (Anderson, 1996). Another HCl CEM system is installed at a resource recovery facility in New Jersey in response to a permit requirement (Ballay, 1996). FTIR monitoring systems are installed and reporting data at a hazardous waste incinerator in New Jersey. Additionally, a prototype gas chromatograph continuous monitoring system measuring multiple organic compounds is installed at a printing facility in North Carolina (Davis, 1996). Some of these installations, and many others, are installed on a trial basis; future requirements may depend on the experience that is gained in these efforts.

Three example state/regional initiatives are described below which represent a range of CEM applications and programs. These examples differ from the previously described federal regulatory programs and illustrate alternative approaches, performance specifications, problems, and solutions that may be useful in other applications.

2.2.1.1 Pennsylvania Non-Criteria Pollutant Monitoring

The Commonwealth of Pennsylvania has taken a somewhat unique approach to the development and implementation of CEM requirements. Pennsylvania's requirements reflect differences in the technical specifications, performance test procedures, and reference test methods for criteria and non-criteria pollutant monitoring. The requirements are contained in, "Continuous Source Monitoring Manual" Revision No. 6 (Commonwealth of Pennsylvania, 1996).

The Continuous Source Monitoring Manual contains CEM requirements for 1) submittal and approval, 2) recordkeeping and reporting, and 3) quality assurance. The submittal and approval process includes Phase I - Initial application, Phase II - Performance testing, and Phase III - Final approval. Detailed requirements for submission of the initial application are provided; the initial application must be approved prior to initial startup of new source and within six months of promulgation of monitoring requirements for existing sources. Performance Specifications for opacity, SO_2, NO_x, O_2, and CO_2, CO, TRS and H_2S, and HCl monitors are provided. In addition, performance specifications are provided for coal sampling, stack gas flow monitors, temperature rate monitors, "pollutants not listed elsewhere" and "parameters not listed elsewhere." For gas pollutant and diluent monitors, performance specifications are included for 1) relative accuracy, 2) calibration error (three points), 3) 24-hour zero and calibration drift, 4) 2-hour zero and calibration drift, 5) response time, 6) operational test period, and 7) data system accuracy. These are more comprehensive specifications than are included in EPA performance specifications. Unique to Pennsylvania is a requirement to verify the performance of opacity monitoring systems by comparison to visual opacity readings. Also unique to Pennsylvania is the requirement to evaluate data system accuracy by comparing "manual calculations" based on monitoring values with data acquisition system output. Installation specifications establishing span value, range, data recorder resolution (% of span and time), measurement cycle time, frequency of zero and calibration checks, and other requirements are also included. Pennsylvania requirements for HCl monitors and "parameters not listed elsewhere" are reproduced herein as Tables 2-6 and 2-7, respectively.

As with performance specifications, CEM quality assurance requirements in Pennsylvania are somewhat more extensive than federal requirements. For example, three-point calibration error tests are required to be performed each calendar quarter. Detailed procedures are included for establishing the values of the calibration standards used for daily checks and for periodic audits. An annual relative accuracy test is required. Also, annual review of the quality assurance plan and quality assurance results by the source operator is required for every facility. Pennsylvania requirements detail criteria to determine when monitoring data are invalid and additional criteria to identify valid periods of data.

Non-criteria pollutant monitoring required in Pennsylvania includes HCl monitors on municipal waste combustors, TRS monitors at pulp and paper facilities, H_2S monitoring in petroleum refinery fuel gas, and various parameter monitoring applications. As with criteria pollutant monitoring, the data are used to assess monetary penalties for excess emissions

Table 2-6. Pennsylvania Specifications for Hydrogen Chloride Continuous Emission Monitoring Systems

Type	Parameter	Specification
Install	Span Value (nearest ppm equivalent)	2.0 times lowest std or as specified in federal regulations
	Range (ppm)	0 to > = max. expected and (> = 1.25 x highest std.)
	Data recorder resolution (% of lowest std.)	1.0 maximum **
	Data recorder resolution (minutes)	5 maximum **
	Number of cycles per hour (meas. and record)	12 minimum **
	Schedule for zero and calibration checks	daily minimum
	Procedures for zero and calibration checks	all system components checked
	Calibration gas ports	close to sample point
Perform	Relative accuracy in terms of standard	
	either (% of reference method)	20 maximum *
	or (% of standard)	10 maximum *
	or (abs ppm for ppm stds)	5 maximum
	or (abs % for % reduction stds)	2.0 maximum
	Calibration error (% of actual concentration)	5 maximum *
	or (abs ppm)	1 maximum
	Zero drift - 2 hour (% of span)	4 maximum *
	Zero drift - 24 hour (% of span)	5 maximum *
	Calibration drift - 2 hour (% of span)	4 maximum *
	Calibration drift - 24 hour (% of span)	5 maximum *
	Response time (minutes to 95% response)	5 maximum
	Operational test period (hours without corrective maintenance)	168 minimum
	Data acquisition system accuracy, 1-hour avgs (%of lowest std)	1 maximum ***

* Expressed as the sum of the absolute value of the mean and the absolute value of the 95% confidence coefficient.

** Must meet most stringent requirements of other analyzers in CEM system (except temperature).

*** If data recording is digital, expressed as the absolute value of the mean. If data recording is analog, expressed as the absolute value of the mean and the absolute value of the 95% confidence coefficient.

Table 2-7. Pennsylvania General Parameter Source Monitoring Specifications

Type	Parameter	Specification
Install	Span Value (terms of measurement)	2.0 times lowest std or as specified in federal regulations
	Range (terms of measurement)	0 to >=max expected & (>=1.25 x highest std)
	Schedule for zero and calibration checks	daily minimum *
	Procedures for zero and calibration checks	measurement simulation if possible, otherwise signal simulation *
	Calibration point	close to measurement point *
	Data recorder resolution (% of lowest std)	1.0 maximum **
	Data recorder resolution (minutes)	1 maximum **
	Number of cycles per hour (meas. and record)	60 minimum **
Perform	Calibration error (% of actual measurement or simulated signal)	5 maximum ***
	Zero drift - 24 hour (% of span)	2.5 maximum ***
	Calibration drift - 24 hour (% of span)	2.5 maximum ***
	Response time (minutes to 95% response)	equal to recorder resolution
	Operational test period (hours without corrective maintenance)	168 minimum
	Data acquisition system accuracy, 1-hour avgs (% of lowest std)	1 maximum ****

Specifications for parameters not listed elsewhere, based on basic measurements of length, mass, time, temperature, current, luminous intensity or events, or derived from such basic measurements (for instance, volume rate, mass rate, velocity, force, pressure, torque, rpm, voltage, resistance, spark rate, etc.). For use only when specified or allowed by an applicable monitoring requirement, or when necessary to convert data to terms of the applicable standard or operational criterion.

* This requirement may be waived if quarterly recalibration of the measurement device/readout device combination is conducted by National Institute of Standards and Technology (NIST) or by a lab using NIST procedures each calendar quarter.

** Must meet most stringent requirements of other analyzers in CEM systems (except temperature)

*** Expressed as the sum of the absolute value of the mean and absolute value of the 95% confidence coefficient.

**** If data recording is digital, expressed as the absolute value of the mean. If data recording is analog, expressed as the absolute value of the mean and the absolute value of the 95% confidence coefficient.

and for poor CEM performance (i.e., monitor downtime). Penalties for excess emissions depend on both the magnitude and duration of periods when the applicable emission standard is exceeded. Quarterly monitoring reports must be certified by the source operator. Electronic data reporting formats and telemetry protocols are specified also.

2.2.1.2 NESCAUM CEM Guidelines for Municipal Waste Combustors

The Northeast States for Coordinated Air Use Management, (NESCAUM) is an organization supported by a group of eight states: Maine, New Hampshire, Connecticut, Massachusetts, Rhode Island, Vermont, New York, and New Jersey. NESCAUM facilitates projects where the participating states pool expertise and resources to address specific air pollution problems. NESCAUM formed a workgroup to develop CEM guidelines for municipal waste combustors because of the number and impact of these facilities being constructed in the northeastern United States prior to the EPA's promulgation of Part 60 Subpart Ea regulations for these sources. In 1990, NESCAUM published "CEM System Performance Specifications and Quality Assurance Requirements for Municipal Waste Combustors" (Peeler, 1990). This guideline document is significant because: 1) more extensive procedural and technical requirements are recommended than are included in the federal regulations for SO_2, NO_x, CO, and opacity CEM systems, and 2) specific performance specifications and quality assurance requirements are recommended for HCl CEM systems.

NESCAUM CEM recommendations were specifically developed to address technical monitoring problems that are encountered at municipal waste combustors and the needs of the participating states. Technical monitoring problems include low emission levels at the control device outlet and widely fluctuating emission levels (intermittent spikes) in CO and SO_2 concentrations at some sources. Major differences in the NESCAUM performance specifications relative to the existing Part 60 regulations were: 1) requirements that gas CEM systems use calibration gases for drift checks and daily checks, 2) requirements for quantitative determination of the calibration gas values, 3) four-point linearity tests for all gas monitors, 4) an additional minimum absolute accuracy specification was included to reflect limitations of the monitoring equipment, reference methods, and relative accuracy test in certain cases, and 5) cycle time/ response time specifications were added for all monitors. The absolute accuracy specification is a mean difference of 5 ppm (10 ppm for CO monitors) during the relative accuracy test and reflects the collective limitations of monitoring equipment and reference methods. The limitations of the relative accuracy test at low pollutant concentrations also are contained in this specification. This specification is included in addition to the PS 2 relative accuracy specifications of ≤20 percent of the reference value or ≤10 percent of the emission standard for SO_2 and NO_x monitors, and similar limits for CO monitors. EPA subsequently included a 10 ppm mean difference accuracy specification in PS 4A for CO monitors at municipal waste combustors. However, similar revisions to PS 2 or PS 3 were not made.

Along with additional and modified specifications, the NESCAUM CEM guidelines include substantive procedural changes to the performance specification test procedures that address specific problems which have occurred during field performance tests. For example, controversy had arisen regarding the validity of performance test results in cases where monitor vendors performed numerous adjustments during the test period and where "normal operating procedures" had not been established for newly installed CEM systems. The NESCAUM guideline document includes recommendations to resolve these issues by requiring source operators to establish prior to the test; 1) criteria for adjusting monitor calibration, 2) criteria and schedules for routine maintenance, and 3) the frequency and criteria for additional checks of monitoring equipment.

Major differences in the NESCAUM QA requirements relative to the Part 60 regulations are: 1) source operators must develop and submit a preliminary monitoring plan, 2) QA plans are required for all sources and detailed guidance on QA plan content is provided, 3) an annual review of QA plans by the source operator is required, 4) a four-point linearity test is required to be performed each calendar quarter, 5) a relative accuracy test is required once per year and must be performed immediately before or after the quarterly linearity test, and 6) minimum data availability specification (90 percent of source operating time) is included.

2.2.1.3 SCAQMD RECLAIM Program

Since the passage of the 1990 Clean Air Act Amendments, the South Coast Air Quality Management District has been involved in the development of Regional Clean Air Incentives Market, or "RECLAIM" program. This innovative market-based program was developed as an alternative to the traditional "command and control" approach in an

effort to achieve air pollution emissions reductions in a more cost effective and efficient manner. The evolution of RECLAIM and its objectives are discussed by Lents (Lents, 1996). RECLAIM is an example of what has become known as a "cap and trade" program.

A number of fundamental issues addressed in RECLAIM are applicable to other cap and trade programs. These include: 1) determining the exact population of sources included in the program (pollutants, source categories, size thresholds, exemptions, etc.), 2) determining the "cap" or total emissions allowed for pollutants and determining how the cap is to decrease over time to achieve necessary emission reductions, 3) determining how permitted emissions are to be allocated amongst the population of sources initially, and over time, and establishing baselines for historic emissions, 4) determining how emissions are to be measured by the affected sources and monitored by the agency to provide an accurate, reliable, and systematic basis for trades, 5) developing trading mechanisms that would encourage rather than inhibit the process, 6) reconciling the trading program with other applicable regulations for the populations of sources, and 7) changing the procedures used to issue permits and enforce regulations and permit conditions.

RECLAIM originally was intended to apply to emissions of NO_x, SO_2, and VOCs. During the development of the program, SCAQMD decided to postpone the VOC program because: 1) technical difficulties are encountered in attempting to quantify these emissions (few historical quantitative measurements, many small sources and many fugitive emission points), 2) some of the VOC compounds also are classified as hazardous pollutants and thus, different regulatory considerations apply, 3) different VOCs participate to different extents in reactions to form ozone, and 4) the workload associated with the program was too great, even after eliminating consideration of the VOCs. SCAQMD is now attempting to implement RECLAIM for NO_x emissions from 370 facilities and SO_2 emissions from 40 facilities. All of these facilities are required to install CEM systems to quantify their SO_2 and NO_x emissions. Measurement data are averaged and 15-minute values are calculated by remote terminal units at each facility. Data are transmitted electronically to a central AQMD computer. The computer is programmed to deploy an inspector when a problem is indicated at a particular facility.

RECLAIM represents a comprehensive program that deals with many complex issues even for monitoring of criteria pollutants. Even greater technical challenges must be overcome to apply such an approach to non-criteria pollutants.

2.2.2 Compliance Assurance Monitoring (CAM) Program

Before the 1990 Clean Air Act Amendments, EPA and some state and local agencies had concerns that some air pollution sources were not in compliance with applicable regulations resulting in adverse air quality impacts. The 1990 CAAA requires EPA to develop regulations for permitted sources to enhance air pollution monitoring and certify compliance with air pollution regulations. Permit regulations in Part 70 require certain sources to perform periodic monitoring and to submit annual certifications of compliance. In October of 1993, the EPA proposed the Enhanced Monitoring Program (58 FR 54648-54699). This proposed program was to require all major sources subject to federally enforceable requirements to develop procedures and methods that continuously demonstrate compliance with emission standards. Data from enhanced monitoring were to be viewed as "presumptively credible evidence" for use in the enforcement of regulations. Thus, various performance specifications and quality assurance requirements were also proposed. The proposed enhanced monitoring program fundamentally changed the compliance methods for many sources and was expected to impose great financial burden on both regulated sources and air pollution control agencies.

The enhanced monitoring rule was withdrawn in April of 1995 and the EPA subsequently drafted the compliance assurance monitoring program (CAM). The draft CAM rule was released in September of 1995 and a second draft was released on August 2, 1996. (See the EPA TTN BBS, phone 919-541-5742.) According to the accompanying announcement, the CAM program attempts to build on existing regulatory monitoring approaches by focusing on "providing a reasonable assurance of compliance with emission limits by monitoring that ensures control measures are operated and maintained in a manner consistent with good air pollution practices." The CAM rule is intended to satisfy the periodic monitoring requirements in Part 70 and the enhanced monitoring requirements in the 1990 CAAA. According to EPA, the proposed CAM rule will cover about 60 percent of the emission units with control equipment and 20 percent of all other emission units.

Where continuous compliance monitoring is required, the draft CAM rule exempts the source from additional monitoring. For affected units with control equipment, the source must develop and comply with a CAM plan. The CAM plan is to include operating indicator ranges for control equipment that represent good air pollution control practices that minimize emissions. Excursions beyond these indicator ranges trigger prompt corrective action. An excessive duration of excursions requires more intensive evaluation, corrective action, and requires notification to the permitting authorities of potential compliance problems.

The CAM rule does not require sources to install CEM systems, so few sources are expected to do so as a result of this rule. Depending upon the specific requirements included in the final rule, and the outcome of other rule making efforts (such as the "credible evidence" rule), some sources may find opacity or other pollutant monitors advantageous. EPA has indicated that explicit requirements to satisfy enhanced and periodic monitoring of hazardous air pollutants will be included in future Part 63 NESHAP standards.

2.2.3 Open Market Trading

The 1990 CAAA encourages the use of market-based approaches, including emission trading to assist in achieving ambient air quality standards. Market-based trading programs are intended to provide incentives for sources to reduce emissions beyond applicable requirements and encourage early emission reductions and technological innovations to reduce and measure emissions.

Emissions trading systems may be categorized as being either "open" or "closed." Examples of "closed market" programs are the EPA Acid Rain Allowance Trading Program and the SCAQMD RECLAIM program. In closed markets, emission trading is restricted to a defined population of sources, total emissions are limited, or "capped" (which may decrease with time to achieve overall reductions), and portions of the total allowed emissions are allocated among the affected sources.

In contrast, open market trading programs involve voluntary participation, may include diverse types of sources, and are designed to be compatible with existing regulations. These trading programs typically involve the exchange of discreet, quantifiable emission reduction credits between sources with some portion of the reduction "retired" to provide for improved air quality. Open market trading programs also may involve banking of emission reductions for use at a future date. The fact that open market trading allows for the exchange of emissions both over time and between sources distinguishes this approach from emissions averaging between sources. Open market trading programs may be very flexible and avoid many of the problems associated with establishing baseline emissions and allocating emission allowances among a specific population of sources.

On July 26, 1995, the EPA administration signed "Open Market Trading Rule for Ozone Smog Precursors: Proposed Policy Statement and Model Rule (USEPA, 1995b)." The preamble discusses many aspects of open market trading approaches as they apply to NO_x and VOC monitoring. An important aspect of these programs are the measurement protocols used to quantify the discreet emission reductions (DER) that are bought and sold. The DER must be "real, surplus, and verifiably quantified" according to the preamble of the model rule. Measurement protocols may include a wide range of inputs including emission factors, engineering calculations, periodic source testing, predictive emissions models, and CEM systems. The model rule allows for states to adopt these programs and facilitates their rapid approval by EPA.

Michigan, Texas, New Jersey, New York, and Virginia have developed, or are developing, open market trading programs. NESCAUM/MARAMA, Northeast States for Coordinated Air Use Management/ Mid-Atlantic Regional Air Management Association) have undertaken a project to encourage interstate open-market trading of NO_x and VOC emissions. NESCAUM/MARAMA have developed a series of measurement protocols that involve determining baselines, applying emission factors, and using CEM systems.

The Michigan Department of Environmental Quality (DEQ) has specified some characteristic elements of DERs (called Emission Reduction Credits (ERCs) in Michigan). "ERCs must be:

1) surplus, in that reductions are not required by any applicable requirement;
2) real, in that all emission reductions have actually occurred;
3) quantifiable, in that all reductions can be measured and are replicable;
4) enforceable, in that they can be enforced by both DEQ and EPA; and

5) permanent, in that the reductions were continuous during the time the ERCs were generated."

The viability of open market trading programs for VOCs that rely on continuous monitoring of emissions present several challenges. Where a monitoring system providing a "total response" (as opposed to speciating particular organic compounds) is used, assumptions regarding the composition of the VOC emissions may be necessary to account for varying instrument response factors of the instrument for different compounds. In addition, assumptions are also necessary to estimate the molecular weight used in calculating emissions on a mass basis. Additional considerations apply because many VOCs are also hazardous air pollutants and because emission reduction credits for hazardous compounds can not be applied to achieve compliance with NESHAP (MACT standards). Finally, an equitable basis for the exchange of VOC emission reductions may need to consider that different compounds participate to different extents in reactions leading to the formation of ozone. The decision-maker considering participation in an emission trading program for VOCs or other non-criteria pollutant must seek resolution of these issues with the applicable control agency.

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Chapter 3
Monitoring Technology - Instrumentation

Continuous monitoring of non-criteria gases may require specialized sampling and analysis procedures since the measurement of reactive and condensable gases can be particularly difficult. An understanding of the composition of the stack gas stream, the behavior of the components of interest, and the potential physical and chemical reactions that may occur in the stack or within the sampling system is necessary to understand and gauge the sampling problems that may be encountered.

Sampling approaches used in the measurement of criteria pollutants can be applied to the measurement of hazardous air pollutants if sufficient care is taken. Once a representative sample can be delivered to an analyzer, a number of options are available for measuring the concentrations of organic compounds, particulate matter, and metals. Approaches to both sampling and analysis are discussed in this chapter.

3.1 Monitoring Systems for Non-criteria Gases

Solutions to sampling problems for non-criteria gases are offered to varying degrees by different system configurations including hot/wet extractive systems, dilution systems, close-coupled systems and in-situ monitoring systems. Each configuration has its strengths and weaknesses. The sampling system chosen must be compatible with the analytical instrumentation used to measure the gas concentrations. Selection of both the sampling and analytical systems will depend greatly on the chemical characteristics of the pollutant.

3.1.1 Sampling Problems For Reactive and Condensable Gases

Reactive and condensable gases such as HCl, NH_3, and formaldehyde present great measurement challenges. Such gases may react with other components within the stack gas stream; they may condense or be absorbed by liquid condensate within an extractive sampling system, they may adsorb onto surfaces, or they may polymerize before reaching the analyzer. Where these and other related phenomena occur, measurement results will be affected. The extent of these effects range from introducing bias into the data to completely invalidating all measurements. Continuous monitoring of reactive and condensable gases is much more difficult than monitoring of criteria pollutants. Depending upon the components making up the flue gas stream, special sampling equipment may be needed and special operation and maintenance procedures may be required to achieve reliable results.

3.1.1.1 Surface Adsorption

Different compounds may adsorb onto the surface of various materials within the sampling system components and therefore be removed from the sample stream before reaching the analyzer. The extent of the adsorption depends on many factors, including: the physical properties of the compound of interest, the gas concentration of the analytes and interferences, the type of material comprising the adsorption surface, the amount of exposed surface area, the surface condition, the gas and surface temperatures, and the time needed for the adsorption process to reach equilibrium. The effects of many of these factors are interdependent and vary with age and previous use (or abuse) of the sampling system.

The selection of appropriate sampling system materials is important in minimizing the adsorption of many compounds. In general, selection of inert materials minimizes adsorption but several other factors must be considered. For example, measurement of ppm levels of criteria pollutants such as SO_2 and NO_x usually can be accomplished with sampling system components fabricated of high quality stainless steel, Teflon, or glass. In many applications, Teflon is viewed as a completely inert material. However, less adsorptive materials, such as poly ether ether ketone (PEEK) may be required for tubing used in measurement applications of ppb level of organic compounds. Similarly, the use of Teflon is not recommended for measurement of "organofluoro" compounds because they are chemically similar to the Teflon polymer and may result in a positive measurement bias. Also, studies have been performed that demonstrate that certain materials can permeate Teflon (Dunder, 1995).

In general, increasing the surface temperature of a solid will reduce gas adsorption on the solid. Heat transferred from the surface increases the internal energy of the adsorbed molecule helping it to overcome the weak molecular attraction and escape from

the surface. For highly adsorptive gases, sample lines may be operated near the physical temperature limits. However, for some compounds such as CO, permeation through the walls of Teflon tubing occurs to a greater extent at higher temperatures.

The presence of "active sites", e.g., irregularities in a material surface at the molecular level, provides locations for chemisorption or the formation of weak chemical bonds with gas molecules that significantly affect the adsorption of gases. In the measurement of low concentrations of organics, highly polished stainless steel vessels with thermally deposited nickel are used to minimize the effects of adsorption. The virgin surface is virtually free of active sites and good sample recovery efficiencies have been obtained for many compounds. When small amounts of moisture are present in the samples less adsorption will occur. Speculation is that the water molecules preferentially occupy the reactive sites and thus minimize adsorption of other analytes. Similarly, improved recovery efficiencies have been observed in the presence of 2 percent moisture by volume (Peeler, 1996).

Surface corrosion, due to the deposition of acids or other factors, creates many active sites in metal surfaces and greatly changes the adsorptive effects of the surface for many compounds. The potential for degradation of a sampling system over time is great because stack gases often contain significant concentrations of sulfuric, nitric, hydrochloric, or other acids. A sampling system that initially performs very well may be rendered completely incapable of transporting HCl to the analyzer due to corrosion caused by the accumulation of condensate within the system. In addition, deposits of particulate matter on filters or other surfaces within the sampling system may increase adsorption greatly. For these reasons, the age and history of use of a sampling system affects its performance. Therefore, periodic checks of the sampling system are required.

Variations in the gas concentration, or changes in other parameters, affect the adsorption equilibrium resulting in subsequent increased adsorption or desorption of the compound of interest. Adsorption affects the response time of an extractive sampling system; the greater the adsorption, the longer the time required for a measurement system to display a stable and fully equilibrated response to a step change in gas concentration. The effects of adsorption may sometimes be determined through response time tests using dry calibration gases. However, as discussed above, the adsorption also may be affected by the presence of moisture or other components in the stack gas samples. Small unswept volumes within the sampling system (e.g., calibration injection lines) can mimic the effects of adsorption by allowing analytes to diffuse during sampling, thus confounding attempts to quantify adsorption. Because sampling systems often are fabricated of many components and different materials, isolating adsorption problems can be quite difficult.

3.1.1.2 Solubility and Condensation

The stack gas streams at stationary sources contain compounds that will condense if the sample temperature is reduced. Depending on the type of sampling system that is used, water vapor may condense as the sample temperature is lowered. Other compounds, such as sulfuric acid, may condense along with water vapor to form acid condensate, or sulfuric acid may condense even when the sample temperature is maintained above the moisture dew point. Condensate formed by cooling stack gas samples can be a complex mixture of substances. This condensate may be detrimental to the sampling system materials and cause corrosion or other problems.

Some compounds, such as HCl and NH_3, are highly soluble in water. The presence of condensate within the sampling system will scrub water soluble compounds such as HCl. Obviously, if HCl is the compound of interest, the presence of condensed moisture in the sampling system will invalidate measurements. In other cases, where measurements of insoluble compounds are made in a sample stream that contains HCl, the presence of condensed moisture in the sampling system may protect the analyzer from damage. Thus, a decision to use a condenser system to remove moisture depends on the solubility of the compound of interest and other materials present in the stack gas matrix.

Industrial process emission streams will reflect a wide range of moisture contents, depending on the nature of the process and the type of control equipment that is installed. The moisture content that will be encountered in a particular application must be known; 1) to size condensers or dryers used for moisture removal, 2) to select an appropriate dilution factor to maintain the sample above its dew point, or 3) simply to gauge the significance of the problem. The moisture content of combustion source exhaust streams typically ranges from 8 to 20 percent by volume depending on the fuel combusted. Hazardous waste incinerators with quench towers and spray dryers may have emission streams containing as much as 50 percent water. Portland cement kiln exhaust streams are likely to contain moisture ranging from 10 to 35 percent by volume depending on the type of process (i.e., dry process, precalciner or wet process kiln). On the other end of the spectrum, sulfuric acid plants will have no moisture at all in the stack gas. The moisture

content may be estimated based on knowledge of the process or it may be measured directly over the range of process/control equipment operating conditions.

The absorption of a somewhat water soluble component will reach an equilibrium between the liquid and gas phases given sufficient time and a constant concentration of the component in the gas phase. (This is not the case where chemical reactions with other components occur in solution.) However, most sampling systems form new condensate continuously, and the concentration in the gas sample may also change with time. Therefore, the application of equilibrium solubility constants may be inappropriate, or at best, an indication of a one-sided limit for estimating the extent of this phenomena. The design of condensers in extractive systems should minimize contact of the condensate and the sample stream to minimize the absorption of slightly water soluble compounds. That the condensate not be allowed to accumulate is also important; it should be continuously removed to minimize absorption of soluble compounds and opportunities for reactions with other stack gas constituents.

Solubility losses of many pollutants are understood poorly. VOC or organic hazardous air pollutant monitoring applications may contain mixtures of soluble, slightly soluble, and insoluble components. Little quantitative information is available in the literature. A few studies at hazardous waste incinerators and sewage sludge incinerators have indicated that heated sampling systems with total hydrocarbon (THC) analyzers measure higher concentrations of volatile organics than systems that include refrigerant moisture removal systems (Cone, 1989). Thus, some regulatory applications specify the use of a heated system even though operational problems are reduced extensively with a "cold" system. Unfortunately, the identity of the specific compounds that are removed in a water condenser and the degree to which they are removed are largely unknown because THC systems provide no information about the individual organic species that are present.

A few studies have been performed using condensers with either FTIR or GCMS analyzers where a variety of organic compounds were dynamically spiked into sample streams (EPA, 1993; Peeler, 1996). The investigators of these studies have demonstrated acceptable sample recovery efficiencies for certain water soluble compounds in the presence of 8 to 35 percent water vapor. (See Chapter 7 discussions regarding dynamic spiking procedures.)

3.1.1.3 Chemical Reactions

Chemical reactions can occur between various stack gas components resulting in the formation of new chemical species. Because of the complex nature of some stationary source emissions, it is difficult to determine the extent of these chemical reactions. Polymerization, neutralization, and sublimation/condensation reactions are suggested frequently by scientists, engineers and technicians as causing sampling and analytical problems. Many undocumented myths exist about the various chemical reactions both within the stack and within the sampling system. Determining whether chemical reactions occur in the stack or in the sampling system when performing extractive testing is very difficult, because the analyzer only detects what the sampling system can deliver. Detection of chemical reactions that occur within the source virtually are impossible to determine because some species are short lived, while others reach a state where the products of the chemical reaction are in equilibrium with the reactants.

Polymerization Reactions. Polymerization reactions are those that occur when a compound reacts with itself (or a similar compound) to form a large molecule. An example of this phenomena is the reaction of formaldehyde with itself to form paraformaldehyde. Paraformaldehyde is a solid that may be formed in sampling systems where cold spots exist. Individual formaldehyde molecules react with each other at the surface of these cold spots to form a polymer layer. This deposition results in a negative measurement bias for formaldehyde. The results of polymerization reactions manifest themselves in a manner similar to surface adsorption.

Neutralization Reactions. Neutralization reactions are those reactions that have a net effect in reducing an acidic or basic component in the stack gas. In the pure sense, neutralization reactions usually occur in solution where hydrogen ions (H^+) and hydroxide ions (OH^-) react to form water. In the gas phase, neutralization may occur by solubilization first and neutralization second, or by direct adsorption of components onto particulate matter. The apparent removal of HCl by CaO (lime) in baghouses following spray dryers on the particulate filter cake of a sampling system are examples of this type of reaction. Reaction of HF with silica in glass surfaces to form SiF_4 is another neutralization reaction.

Salt-forming Reactions. Salts can form when two or more gaseous compounds react. An important example is the equilibrium reaction between gaseous hydrochloric acid (HCl) and ammonia (NH_3) to form solid ammonium chloride (NH_4Cl). Both HCL and NH_3 are volatile, non-condensable gases while ammonium chloride is a water soluble solid compound having an exceptionally low vapor pressure. This reaction is

known to occur under atmospheric conditions (Seinfeld, 1986), and may cause either positive or negative measurement biases that are dependent upon the stack gas and sample delivery temperatures.

Another example of a salt-forming reaction is the combination of SO_2, NH_3, and water to form ammonium bisulfate. This reaction can occur in the atmosphere downstream of a source, producing a detached plume and in some cases particulate fall-out. This reaction can also occur within the condenser of a CEM system creating low biases for either SO_2 or NH_3 measurements.

3.1.2 Solutions to Sampling Problems

Extractive sampling systems must be designed and operated in a manner that provide consistently representative samples to the analyzer. The design of the sampling system must eliminate, or at least minimize, any reactions or loss of the analytes of interest before they reach the analyzer. The operation of the sample acquisition and sample handling components must ensure that the necessary conditions are maintained over the complete range of source operating conditions to afford representative measurements of reactive and condensable gases.

3.1.2.1 Hot/wet Systems

"Hot/wet systems" are extractive CEM systems that maintain the sample temperature above its dew point throughout the sampling system and within the analyzer. These systems may be used for the measurement of water soluble compounds and commonly are used for monitoring non-criteria pollutants such as HCl, NH_3, and VOCs. Other compounds can also be measured provided that a suitable heated analyzer is available. Hot/wet systems have been used for many years to monitor criteria pollutant emissions such as SO_2, NO_x, and CO. Important aspects of hot/wet sampling systems for reactive and condensable gases are illustrated in Figure 3-1.

Hot/wet sampling systems must not only maintain the sample temperature above the dew point to avoid condensation, they must also minimize adsorption and avoid the potential for chemical reactions to occur. Consider for example, monitoring of HCl which is 1) very water soluble, 2) adsorbs onto common sampling system materials, and 3) participates in chemical reactions with other stack gas constituents at certain sources. Extractive HCl sampling systems have been used that minimize adsorption effects by operating Teflon sampling lines at temperatures between 350°F and 375°F (the maximum operating temperature for Teflon). High sampling flow rates are maintained (20 liters per minute) and short sampling lines are used in these systems to minimize the residence time and to minimize the surface area for adsorption. Heated head pumps fabricated of 316 stainless steel or other special alloys and with Teflon diaphragms are used to avoid condensation or adsorption. All cold spots within the sampling system such as connections between heated line segments or connections to pumps or manifolds must be eliminated. Nothing less than meticulous attention to ensuring that the entire sample path is heated will prove adequate. The performance of "system calibrations" where calibration gases are introduced at the outlet of the sampling probe are very important for these types of systems to identify and/or account for the effects of adsorption (see Figure 7-5). System calibrations are sometimes avoided in practice because of the high consumption rate of calibration gases (and corresponding cost) due to the high sampling rates and the longer time required to achieve an equilibrated instrument response.

HCl also serves as an example of a chemically reactive component. HCl may participate in chemical reactions with lime or similar materials collected within the sampling system. Special provisions are required to minimize the collection of the particulate matter where a stack gas stream contains solids or liquids that are chemically reactive with the component of interest. Since the reaction of HCl with particulate material is most likely to occur on filters, the equipment must be designed to accommodate system calibrations where calibration gases are introduced upstream of the filters. This may help to detect whether reactions with the particulate matter are occurring. (Procedures described in Chapter 7, Dynamic Analyte Spiking, provide a method to detect such chemical reactions.)

As previously described, HCl may participate in reactions with ammonia to form ammonium chloride salts. As discussed before, this reaction is sensitive to the sample temperature. Where the sample temperature within the analyzer is substantially below the stack gas temperature, the reaction may consume HCl and thus introduce a negative (low) bias in the HCl measurement results. Conversely, where the measurement system is maintained at a higher temperature than the stack temperature, particulate ammonium chloride may volatilize to form HCl and NH_3 thereby creating a positive bias in HCl monitoring results. The potential for such biases to occur at particular sources, and the effects of temperature changes between the stack and the analyzer, must be examined for hot/wet measurement systems.

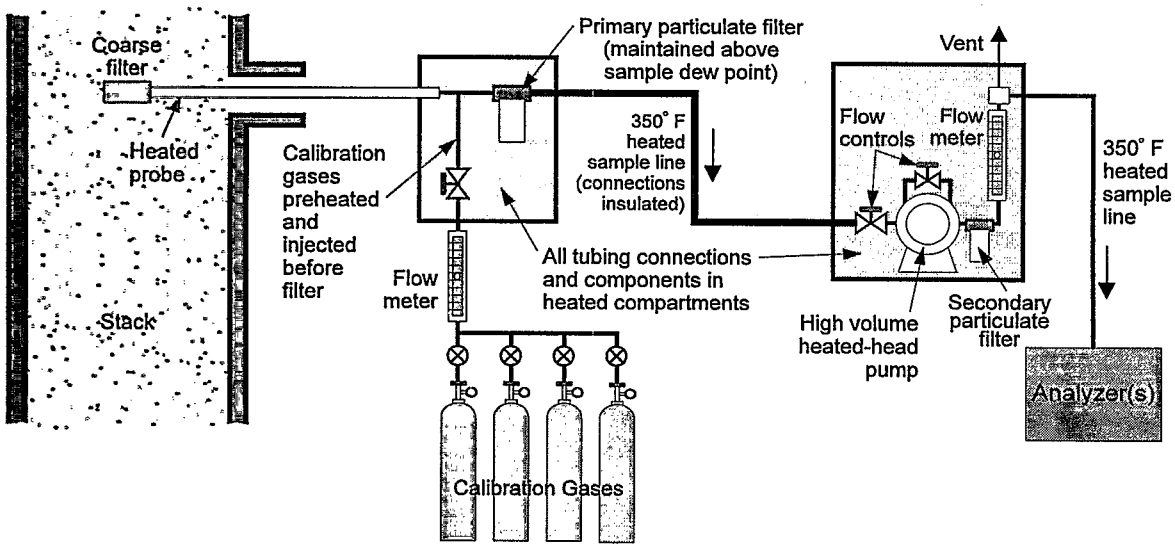

Figure 3-1. Hot/wet sampling systems.

3.1.2.2 Dilution Systems

Dilution systems quantitatively dilute stack gas samples with clean dry air to reduce the relative moisture content so that the sample is maintained above the dew point with little or no heating. Because moisture condensation is eliminated as a potential problem, heated sample lines and manifolds can be replaced with simpler, less expensive components. Sample gas condensers or permeation dryers are eliminated also. Usually an aspirator or eductor is used to move both sample and dilution gas thus, eliminating the need for a sample pump. On the other hand, clean-up systems to remove moisture, CO_2, oil, hydrocarbons, or other components from the dilution gas may be necessary.

In-stack dilution probes use critical orifices to control sample flow rate and aspirators to both draw stack gas through the critical orifice and supply dilution air (Figure 3-2).

The critical orifice in the dilution probe ensures that the sample extraction rate is independent of the aspirator vacuum thus providing a constant sample flow rate and consistent dilution of the sample gas. Calibration gases are introduced upstream of the critical orifice and are diluted in exactly the same manner as stack gas samples. In-stack dilution probes are available from many manufacturers and have been used widely in monitoring criteria pollutants, particularly in the acid rain program. Dilution ratios ranging from

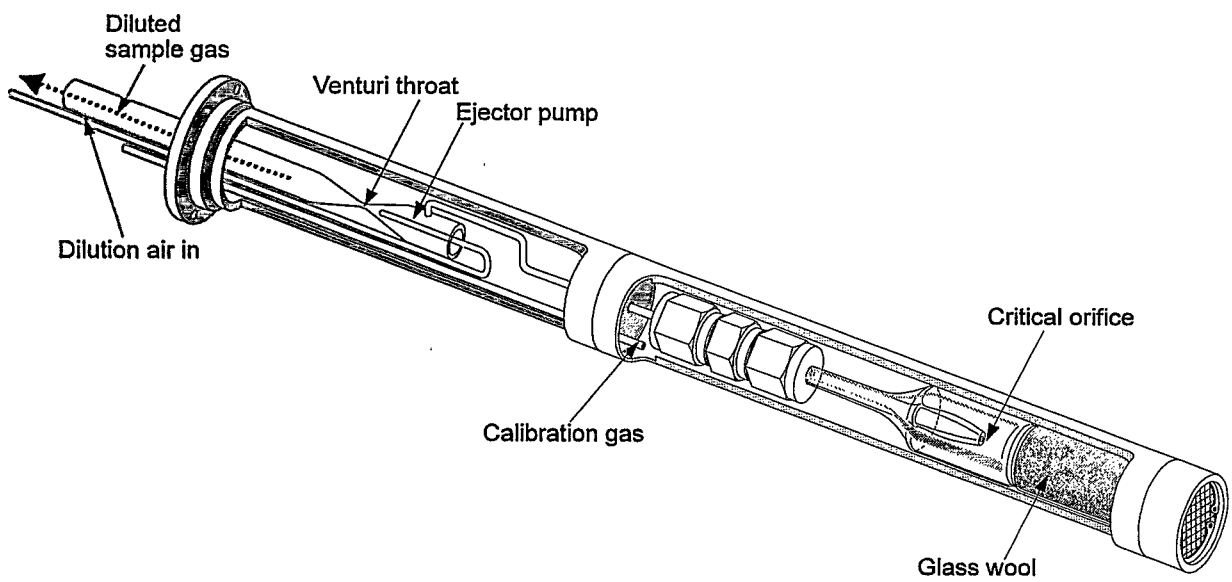

Figure 3-2. In-stack dilution probe.

20/1 to 1,000/1 are used in practice. Analyzers that were developed originally to monitor SO_2 and NO_x concentrations in ambient air are used for emission monitoring in the acid rain program.

Variations in the sample dilution ratio, and resulting biases in monitoring results, may occur where in-stack dilution probes are subject to varying stack temperature, pressure, or molecular weight. These effects have been characterized by Jahnke (Jahnke, 1994a). Newer designs of dilution systems have located the critical orifice and aspirator outside of the stack in a temperature controlled region to minimize the effects of stack gas temperature variations on the dilution ratio (Figure 3-3).

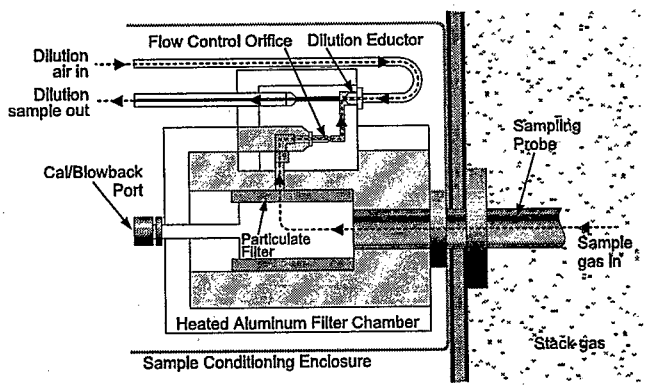

Figure 3-3. Out-of-stack dilution system.

A dilution sampling system is not appropriate where an analyzer with the requisite sensitivity is not available to reliably measure the diluted samples. Usually, the minimum dilution ratio is determined based on the maximum expected moisture content of the stack gas and the minimum temperature in the sampling system or analyzer. Applying this dilution factor to the expected stack gas concentration provides an estimate of the required measurement range. An analyzer with sufficient sensitivity, resolution, and signal-to-noise capability must be available for this operating range. The analyzer must be designed for the specific measurement range; incorporating measurement cells with sufficient optical path length and appropriate filters, detectors, and other devices necessary for the measurement level. Simply increasing the electronic gain of an analyzer does not always change the measurement range.

Problems with adsorption may be encountered with dilution systems even though condensation of moisture is avoided. EPA studies to evaluate HCL dilution system performance at municipal waste combustors and at hazardous waste incinerators demonstrated very slow response times that were attributed to adsorption of the HCL on Teflon sample lines (Shanklin, 1989). The use of heated sample lines can improve the system response times and can provide additional protection against condensation in applications where extremely cold ambient temperatures are encountered. However, one of the major advantages of using a dilution system is lost if heated sample lines are required.

The accumulation of organic material within the aspirator of an in-stack dilution probe has been observed during monitor evaluation tests at a power plant in Virginia. This was attributed to localized condensation occurring because of cooling by the dilution air. Pre-heating of the dilution air eliminated this problem. In addition, condensation of acids may occur in dilution sampling systems even though condensation of moisture is avoided. Accumulation of sulfuric acid has been observed in unheated dilution sampling lines at coal-fired electric utility boilers.

One of the major advantages of dilution sampling systems is that they minimize the volume of sample gas extracted from the stack and thereby minimize the contamination of the system by particulate matter. The frequency of replacing filters and other maintenance activities is reduced for dilution systems because less particulate matter is introduced to the system. Nevertheless, the relative amounts of particulate matter and gases extracted is the same for dilution and conventional extractive systems. Therefore, the potential for chemical reactions or adsorption between gases of interest and the particulate matter is not reduced.

3.1.2.3 Close-Coupled Systems

Close-coupled systems minimize extractive sampling components by effectively placing the measurement sensor in close proximity to the sampling point. Many of the problems observed in other extractive sampling systems are eliminated. Close-coupled systems have been developed for the measurement of criteria pollutants (Mandel, 1995). Close-coupled systems also have applications in monitoring non-criteria air pollutants particularly reactive and condensable gases. Several fundamentally different configurations have been developed.

Close-coupled systems have been developed that use FID detectors in "total hydrocarbon" monitoring systems as shown in Figure 3-4. In this example, the heated FID is located in a thermally controlled enclosure just outside the stack wall. The sample is conveyed only a very short distance, thus the surface area for adsorption/desorption reactions and the time allowed for reactions to occur before the sample

reaches the detector are greatly minimized. This design allows for rapid responses of the measurement system and minimizes sampling system maintenance.

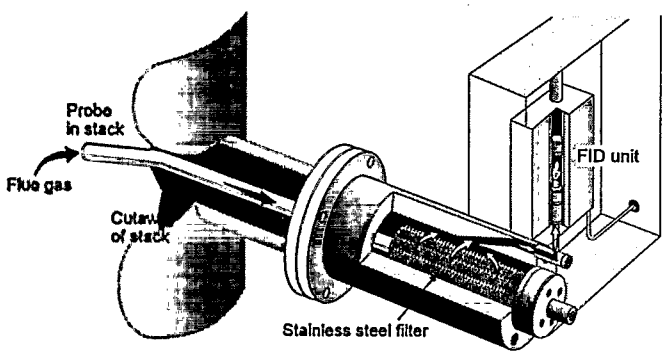

Figure 3-4. Close coupled system.

Close-coupled systems have been developed that use "reactive gas analyzers" for the measurement of NH_3, SO_3, and H_2SO_4. These measurement systems incorporate a means of contacting the sample gas stream with an absorbing solution at the outlet of the sampling probe. The absorbing solution may simply absorb the compound of interest or it may facilitate chemical reactions which convert this component to a more stable form. The chemical solution is continuously renewed and after exposure to the gas sample it is conveyed some distance to an analyzer which provides for the determination of concentration. This approach provides for the immediate reaction of the component of interest, and possibly the selective chemical removal of interfering species, to make the measurement. Many of the precautions evident in other systems that are necessary to avoid condensation, minimize adsorption, or avoid chemical reactions are not needed in this approach.

Another close-coupled system configuration has been introduced which uses a solid state tunable diode laser analytical method (Frish, 1996). This technique is capable of measuring many components in the infrared spectrum and can be used for monitoring NH_3, HF, H_2S and other toxic gases. In these systems, the laser source and photodetectors necessary for the measurement are contained in a control module at a remote convenient location as are analyzers in extractive monitoring systems. A fiber optic cable is used to connect the control module to a sample probe. The probe provides for the continuous flow of stack gas through an optical cell mounted in a thermally controlled chamber immediately outside the stack as shown in Figure 3-5.

Because this measurement system can employ fiber optic cables as long as 1 km, the advantages of a close-couple optical measurement cell and the convenience of a remote analyzer are provided. In addition, a number of sample probes can be connected to the same control module thereby offering additional cost savings for applications where measurements are required at several locations.

3.1.2.4 In-Situ Measurement Systems

In-situ systems for the measurement of gases sense the concentration of the gas of interest within the stack by either placing a detector within the stack or by projecting a light beam through a portion of the stack gas stream and analyzing various spectral phenomena. Point in-situ systems measure the concentration at a specific point or over a relatively short path length through the stack gas. Cross-stack systems project a light beam across the stack. These systems may be either single pass or double-pass systems depending on whether the light source and detector are on the same or opposite ends of the light path. A double pass system is illustrated in Figure 3-6.

In-situ systems for measurement of criteria pollutants are described by Jahnke (Jahnke, 1993). Regardless of the configuration, all in-situ systems must be designed to determine the concentration at stack conditions, which typically involves varying temperature, pressure, and moisture content. Other factors, such as particulate loading or the concentration of interfering gases, also vary and may affect the measurement process or accuracy of results.

An advantage of in-situ systems is that many of the sampling problems associated with extractive systems are eliminated. Assuming that the stack gas temperature is above the dew point, condensation is not an issue. Adsorption of gases is irrelevant. Reactions between gases and particulate matter can be ignored for all in-situ systems except for those that use a thimble or filter to protect an in-stack detector. In-situ analyzers are particularly appropriate, and in some cases, the only option for the measurement of reactive and condensable gases because the influences of the extractive sampling system are eliminated.

On the other hand, in-situ analyzers may need to compensate for variations in gas density due to temperature or pressure variations, variations in spectral absorption due to temperature shifts, as well as variations in particulate matter loading and the presence of other interfering species. The method used to

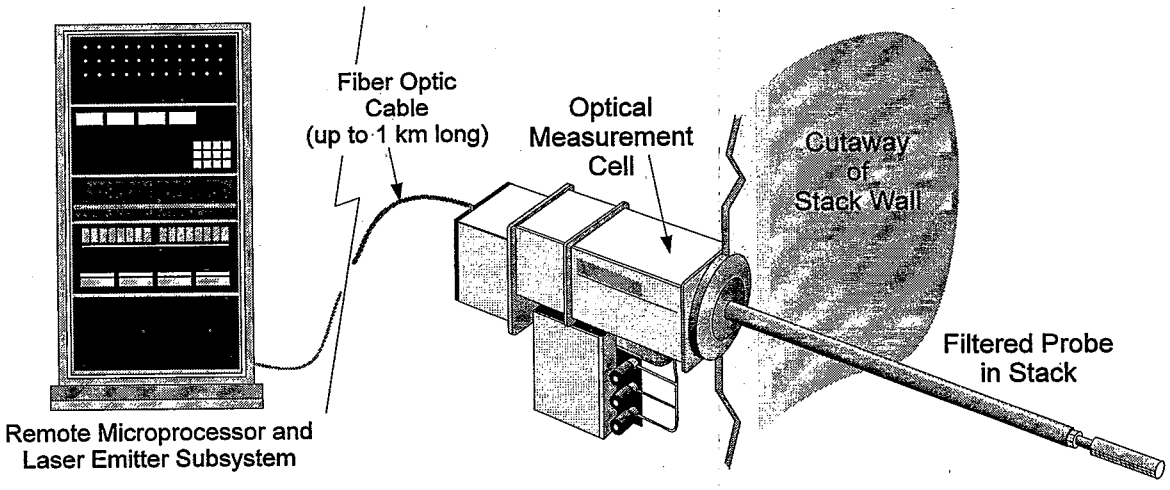

Figure 3-5. Close-coupled laser monitoring system.

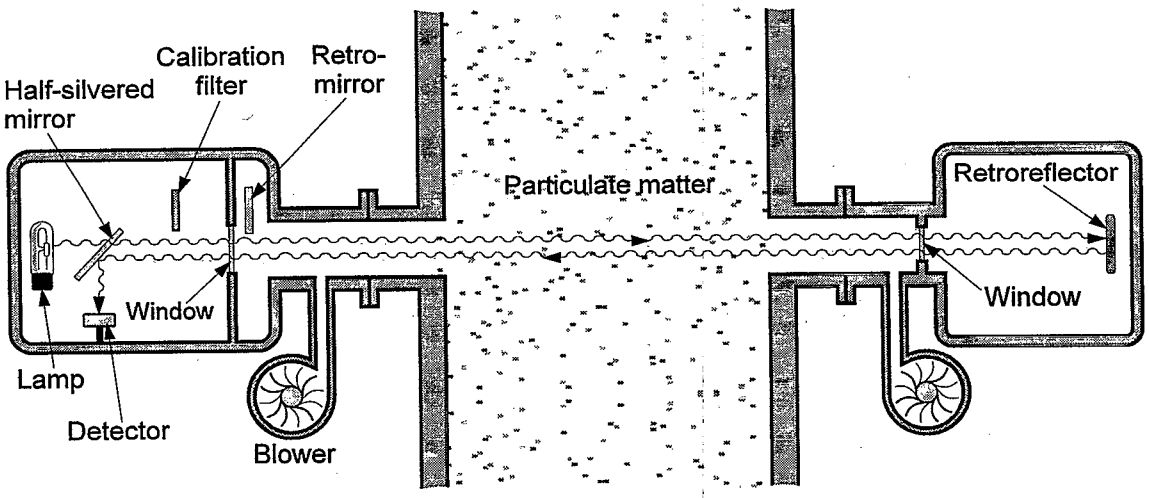

Figure 3-6. Double-pass transmissometer.

compensate for these types of factors is inherent to the analytical technique. Consider for example, an optical infrared dispersive device. Variations in the effluent temperature change the gas density and thus the number of molecules present in the adsorption path at a particular concentration. Sensing of the effluent temperature is necessary to distinguish between changes in infrared adsorption due to concentration variations or due to temperature variations. Also, the actual spectral adsorption of infrared radiation varies as a function of temperature for different compounds. Thus, effluent spectra and reference spectra obtained at the same temperature must be "matched" in order to analyze the data accurately.

Temperature compensation for spectral adsorption can be performed by obtaining a series of spectral libraries at different temperatures on a controlled calibration facility. This approach has been used for infrared gas filter correlation devices and UV differential adsorption instruments. A different approach has

been developed for dispersive infrared measurements that relies on HITRAN reference spectra and mathematical transformations to adjust the reference spectra to correspond to the effluent temperature (Lang, 1991).

A major challenge for in-situ analyzers is the ability to verify proper calibration while the instrument is installed. Because the effluent is present, determining if the zero concentration value is correct is difficult. Various schemes have been used to attempt to overcome this problem. Calibration at saturation (very high concentration) rather than at zero, incremental calibrations superimposing gas filters and the effluent gas, and using concentric slotted pipes or other mechanical means to temporarily provide a zero calibration have all been used with varying degrees of success. An in-situ monitor with a slotted probe for effluent measurements and gas audit cell to facilitate quality assurance checks using external calibration gases has been developed. The probe design ensures that calibration gases are at the same temperature as the effluent gases for reasons previously discussed. Another single-pass cross-stack in situ analyzer uses a zero pipe to provide a reference optical path, free of adsorption, and a flow-through gas cell to facilitate the introduction of calibration gases. This instrument is an ultraviolet differential absorption instrument that can measure many gases including SO_2, NO_x, H_2O, NH_3, volatile organic compounds, and Hg (vapor).

In-situ devices typically isolate optical components from the effluent stream by using optical windows and an air-purge system that provides a flow of filtered ambient air across the optical surfaces and then into the stack. The analytical technique must be insensitive to any dust accumulation on the optical surfaces; otherwise, the decrease in light transmittance might be interpreted as an increase in pollutant concentration. The sample interface system must be adequate to ensure that dust accumulation is held to acceptable levels between maintenance intervals. Otherwise, the intensity of the optical beam may be diminished to the point where deterioration in signal to noise levels reduces the accuracy of the measurement results. Optical windows must be fabricated of materials that transmit the measurement wavelengths and are resistant to chemical reactions and mechanical deterioration.

3.1.3 Analytical Techniques

The analysis of hazardous air pollutants (HAPs) is not as straightforward as the measurement of the inorganic, criteria pollutants such as SO_2 and NO_x. Because of the wide variation of properties associated with the different classes of HAPs (organic compounds, metals, particulate matter), numerous methods are used to analyze the flue gases after they are sampled by the extractive or in-situ systems. These include gas chromatographic methods used for analyzing organic and inorganic compounds, light absorption and scattering methods used for particulate monitoring, and atomic emission spectroscopic methods used for the analysis of metals.

Due to the difficulties of analyzing multiple hazardous air toxic materials in a flue gas matrix, chromatographic separation techniques often are employed to separate compounds in a gas mixture. Compounds can then be measured individually by some type of detector, such as a flame ionization detector (FID), thermal conductivity detector (TCD), photoionization detector (PID), or electron capture detector (ECD). Other techniques where separation of the gaseous compounds is not performed, such as Fourier transform infrared (FTIR) spectroscopy, ideally identify and quantify all of the compounds in the sample at the same time. A combination of separation and analytical methods such as gas chromatography and mass spectrometry (GCMS) can also provide for a versatile analytical system. This section contains a review of hazardous air pollutant monitoring methods that are commercially available, describing principles of measurement.

3.1.3.1 Gas Chromatography

Gas chromatography typically is used to isolate the individual components of a mixture of organic and inorganic compounds from each other for subsequent identification and quantitative analysis. Chromatographic separation principles are used in EPA reference methods (EPA, 1996b). For example, a detailed gas chromatographic procedure is specified in EPA Method 106 for vinyl chloride, EPA Method 16 provides for the chromatographic separation of four total reduced sulfur (TRS) compounds, and Method 18 gives general sampling and analytical criteria for gas chromatographic testing. The use of gas chromatography for CEM regulatory applications has been limited; however, many installations are found in the process industries where the equipment is used to monitor production operations (Villalobos, 1975; Coleman, 1996). Particularly in the refining and chemical industries, resources necessary to provide for continuous, accurate data are made available because of the importance of that data for determining process efficiencies.

3.1.3.1.1 Basic Principles of Gas Chromatography. Gas chromatography is based on the selective distribution of compounds between a stationary phase and

a mobile phase (carrier gas). In this process, the moving gas phase passes over a stationary material that is chosen to either absorb or adsorb the organic molecules contained in the gas. In gas chromatography, the stationary material or phase can be either a liquid or a solid and is contained in a long, thin tube referred to as a "column." Columns are made of fused silica, glass, or stainless steel and vary in diameter depending upon the type of column packing (the stationary phase) used.

In an ideal column operated under ideal conditions, each molecular species will exit the column at a different time. The equilibration between the individual compounds and the column stationary phase is a function of 1) the compound's affinity for the stationary phase relative to the mobile phase, 2) the temperature of the column, and 3) the flow rate of the mobile phase carrier gas. Individual molecules are separated in the column by undergoing a series of equilibrations between the stationary and mobile phases (Giddings, 1965). Selecting the appropriate column and optimizing the column temperature and carrier gas flow rate should enable separation of the gas sample into its individual components.

3.1.3.1.2 Gas Chromatograph Components. A simple chromatographic system is composed of a device for injecting the sample into the column, a carrier gas to sweep the sample gas through the column, a column oven, and a detector. The carrier gas, such as helium or nitrogen, sweeps the sample from the injection area into the heart of the system, the column. The detector at the end of the column ultimately produces an electrical signal that is proportional to the quantity of molecules present (Figure 3-7).

Separated peaks are identified and quantified by comparison of their peak areas to a calibration with known gas standards. However, for an unknown sample mixture, one will not know what standards to include in the calibration unless some prior knowledge of the flue gas composition is available. In that case, one must use techniques such as infrared, ultraviolet, or mass spectrometry to first identify the compounds and then select the column and appropriate standards.

3.1.3.1.3 Detectors. The separation performed in a chromatographic column is sensed by a detector and recorded. Any detector designed for use in a gas chromatograph system must have a high sensitivity for low concentrations of organic molecules, and a rapid response time. Many detectors are available that meet these requirements; the most common in source monitoring applications are the flame ionization detector (FID) and the photoionization detector (PID). In more sophisticated applications, optical spectroscopic or mass spectroscopic techniques are employed.

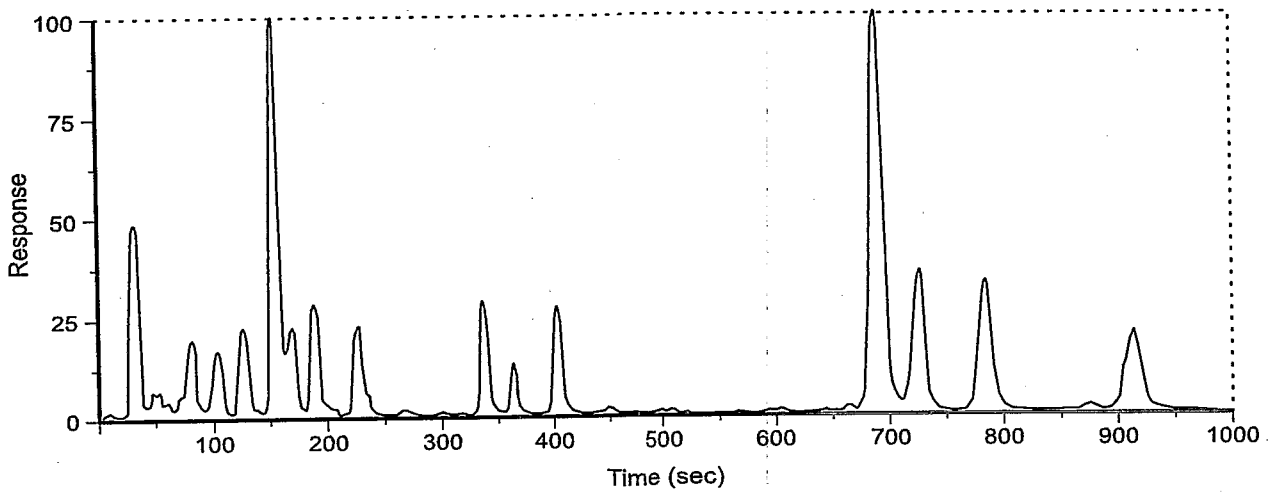

Figure 3-7. Gas chromatogram.

Flame Ionization Detectors. The flame ionization detector is capable of sensing most organic compounds and, because of its relatively high sensitivity, has become widely used in environmental applications. In an FID assembly, the column effluent enters the base of the burner, is mixed with hydrogen, and the mixture burned in a jet with oxygen at a temperature of about 2,100°C. Ions and free electrons are produced by the flame, which increases the current sensed by an electrometer. The current is approximately proportional to the number of carbon atoms entering the flame. However, the response of the detector is slightly different for different types of organic compounds. As a result, the detector must be calibrated for the compounds being studied to achieve the best accuracy (Figure 3-8).

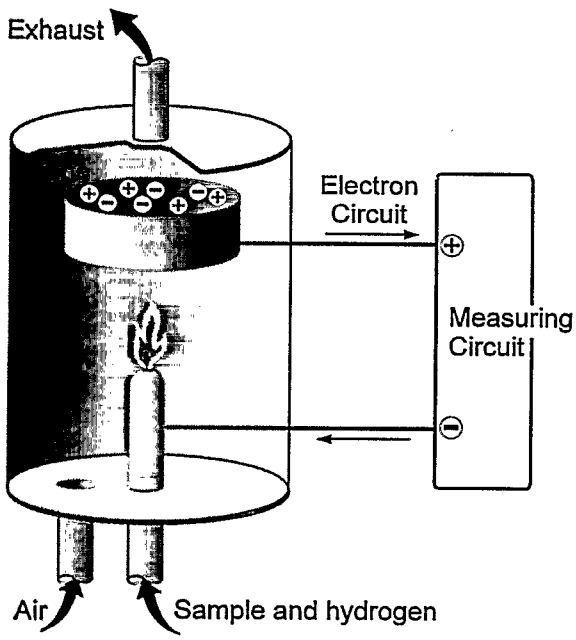

Figure 3-8. Flame ionization detector.

The FID is convenient to use in source sampling situations since it does not respond appreciably to gases such as O_2, N_2, H_2O, CO, SO_2, and NO. However, organic compounds that contain nitrogen, oxygen, or halogen atoms may give a response reduced from that seen from hydrocarbons. In a photoionization detector, organic molecules are ionized by ultraviolet light:

$$R + h\nu \rightarrow R^+ + e^-$$

where R^+ is the ionized organic compound and $h\nu$ represents the energy of the light having frequency ν (h = Planck's constant).

Photoionization Detectors. A typical PID incorporates a UV lamp suitable for ionizing the analytes of interest and a pair of electrodes to measure a current proportional to the concentration. Again, the major components of the flue gas such as O_2, CO, N_2, CO_2 and H_2O are not ionized.

PIDs are used in conjunction with gas chromatographs or alone as portable analyzers used in EPA Reference Method 21 for detecting leaks in petroleum refineries (Hellwig, 1986). They offer advantages over FID detectors in that hydrogen is not required and methane (a gas that is not required to be monitored) is not ionized and therefore not detected by a PID (Hewitt, 1981). Depending upon the instrument, compounds detected by PIDs include: aliphatic and aromatic hydrocarbons, halogenated organics, alcohols, ketones, aldehydes, ethylene oxide, vinyl chloride, and inorganic compounds such as arsine, phosphine, and hydrogen sulfide. In general, compounds that have ionizable electrons can be detected.

Electron Capture Detectors. The electron capture detector (ECD) is selective for certain groups of organic compounds such as those containing halogen atoms or nitro groups. The electron capture detector works by using a radioisotope treated electrode that emits high energy electrons as it decays (β emission). The β electrons react with the carrier gas to produce secondary, free electrons which move to a positively charged anode to generate a current through the system. When the nitrogen carrier gas contains electron-absorbing molecules such as the halocarbons, the electric current will be reduced because the flow of free electrons will be reduced by the absorption.

The ECD is more sensitive for specific groups of compounds than is the FID, but the response can again vary from compound to compound. Issues associated with the transport, storage, and disposal of the radioactive material have also been of some concern.

Other Detectors. Other types of detectors are used in chromatographic systems applied to environmental monitoring. Many of these are species specific like the ECD. Among these are the Hall electrolytic conductivity detector (HECD), used for halogen, sulfur, or nitrogen compounds; the flame photometric detector (FPD) used for sulfur or phosphorus compounds; and the alkali flame detector (AFD), used for nitrogen and phosphorous compounds.

Mass Spectrometers used as Detectors. Increasing demands for the analysis of trace levels of toxic

materials require new approaches to increase the resolving power and sensitivity of chromatographic systems. Multiple detector combinations have been used, but combining the gas chromatograph with a mass spectrometer used as a detector offers one of the most powerful combinations for both identification and quantification. This GCMS combination has been the basis for most low concentration testing for many years in air pollution monitoring and is seeing increasing application (Peeler, 1996).

In the technique of mass spectrometry, molecules are ionized by high energy electrons, or by other means (such as chemical or photoionization process), and the resultant molecular ions and ion fragments are separated according to their mass to charge ratio (m/e). This separation produces a "mass spectrum" of the different ions generated from the fragmentation caused by the high energy electron-molecule collisions (Figure 3-9). The mass spectrum is unique to the original molecule, as is an infrared or UV spectrum.

Mass spectrometers are distinguished by the type of mass separator used. Magnetic deflectors, time of flight separators, quadrupole mass analyzers, and ion-traps have all been used. For environmental applications, the quadrupole mass analyzer is used most commonly. In this technique, an oscillating field of electromagnetic energy filters ions having a specific mass to charge ratio (Figure 3-10).

The linear quadrupole mass analyzer operates by oscillating the ions in a radio-frequency field superimposed on the charged cylindrical rods. Most of the ions will oscillate with increasing amplitude and strike the rods, but one set of rod voltage and radio-frequencies will exist where the ions of a specific m/e ratio will be able to pass through to the detector. The radio-frequency or rod voltage is therefore scanned to obtain the mass spectrum.

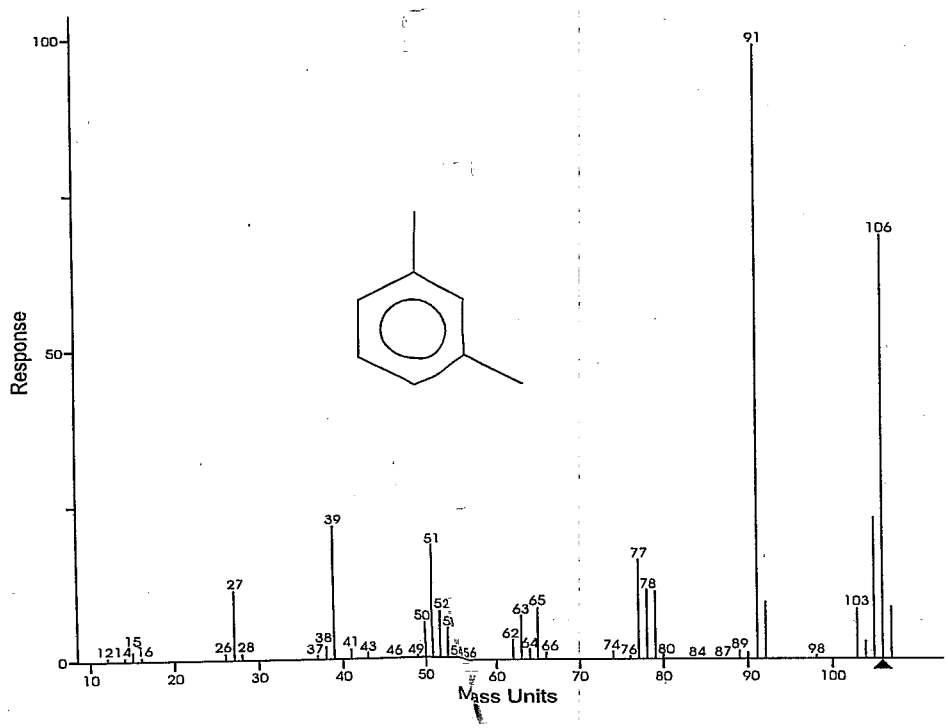

Figure 3-9. Mass spectrum of meta-xylene.

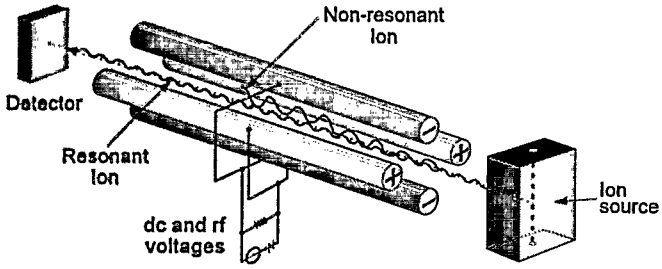

Figure 3-10. Linear quadrupole mass analyzer.

The mass analyzers used in mass spectrometer systems are operated under high vacuum ($1x10^{-5}$ or $1x10^{-6}$ mm Hg) to minimize scattering by collision with other ions and gas molecules. This requires some type of vacuum pump and a system design that can maintain a proper vacuum. The cleanliness of the system is important also, and adsorbed materials on the walls of the analyzer can lead to the introduction of interfering ions. These requirements can lead to problems in source monitoring applications and must be overcome to achieve consistent results.

The GCMS combination provides both qualitative and quantitative information since it looks at each different type of molecule separately as it comes off of the column (Figure 3-11). The GCMS output gives a three-dimensional plot over time, giving information both on the type of compounds in the sample and the amount present.

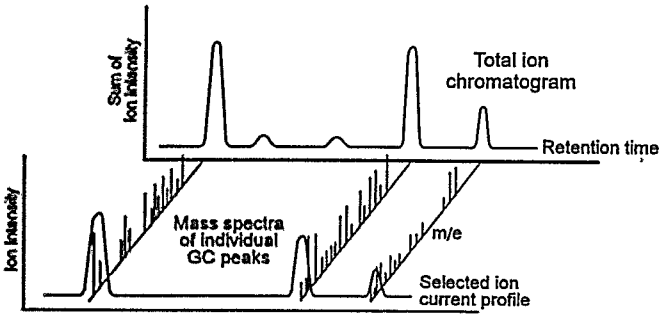

Figure 3-11. Total ion current chromatogram.

Mass spectrometers and GC mass spectrometers have been applied to monitor criteria pollutants on a continuous basis (Bartman, 1990; Harlow, 1990) and are being used increasingly in the process industries to monitor a wide range of HAPs. Their use in environmental monitoring has focused primarily on the ambient monitoring of hazardous waste sites or leak monitoring in the chemical and petroleum industries. However, GCMS systems are being used increasingly in short term source tests to determine baseline HAP emissions (Campbell, 1991; Peeler, 1996). These tests often point out areas where changes in process operational efficiencies can lead to emissions reductions. The design of continuous sampling and operating strategies has been a challenge in many GCMS applications, but these challenges are being met (Kinner, 1993; Haile, 1995).

3.1.3.2 Total Hydrocarbon Analyzers

Depending upon the process and the mixture of compounds present, a preliminary characterization of the emissions frequently is necessary to optimize chromatographic and other instrumentation. The speciation and quantification of volatile organic compounds can be very expensive. Although such knowledge may be useful for process control and optimization, such information is not needed for some facilities, such as incineration sources. In these or other cases, a total hydrocarbon analyzer may be sufficient for monitoring the sum of individual VOC emissions.

Total hydrocarbon analyzers direct the sample to the detector without column separation. The sampling system may be either cold or hot as discussed previously. The hot FID systems provide a more accurate measure of the THC content; however, they are more difficult to operate continuously (see Cone, 1990 for a discussion of this issue). Early hot FID systems frequently incorporated design flaws where organic compounds and water could condense at cold spots in the analyzer plumbing and obstruct the flow of gas or interfere with the control of the sample pressure (Cone, 1990). Such problems are avoided in newer systems.

The FID is the industry standard for total hydrocarbon (THC) analyzers, and is in fact specified as the required detector for use in THC monitoring systems installed in boilers and industrial furnaces that burn hazardous waste and for those installed in sewage sludge incinerators (40 CFR 266). Certification criteria for approving some THC analyzer installations have been simplified by eliminating relative accuracy test criteria and using audit gases to check the system performance (40 CFR 266 Appendix IX and 40CFR 503 Subpart E). These certification criteria are discussed in Chapter 7 of this Handbook.

3.1.3.3 Light Absorption Techniques

Light absorption techniques have been used traditionally to monitor criteria pollutants such as CO, NO, SO_2. The techniques can also be used for the environmental analysis of organic compounds and have been applied extensively both in research laboratories and in process industries. The light absorption

methods are based upon the phenomenon that molecules will absorb light energy to rotate, vibrate, or change their electronic patterns in characteristic ways. This absorption occurs only for wavelengths of light that are in tune with the properties of the molecule (see for example, Willard, 1987).

Light absorption techniques are categorized as being dispersive or nondispersive. In the dispersive methods, the spectral absorption of a molecule is measured over a limited region of the electromagnetic spectrum. A spectral absorption pattern, or spectrum, characteristic of the molecule is obtained that can be used to both identify the molecule and determine the concentration of the molecule in the sample. Scanning spectrometers and Fourier transform infrared (FTIR) spectrometers generate such spectra.

In the nondispersive methods, the so-called nondispersive infrared (NDIR) and nondispersive ultraviolet (NDUV) techniques, the spectrum is not scanned. Here, a wavelength where light energy is absorbed is used as the basis for the instrument design. Such instruments are constructed quite simply.

Differential Absorption Spectroscopy. A typical nondispersive method measures light absorption at two wavelengths, one where the molecule absorbs energy and one where it does not (Figure 3-12).

This particular technique has been called differential absorption spectroscopy or differential optical absorption spectroscopy (DOAS). The ratio of the intensities, I/I_o, at the two wavelengths is known as the transmittance and is related exponentially to the concentration of the gas that absorbs light energy at the wavelength, λ.

In the nondispersive, differential absorption technique, I_o is obtained from the detector when it responds at the wavelength λ_o. In many criteria pollutant monitors, the value of I_o is obtained instead by using a reference gas or reference gas cell that does not absorb light energy at the measurement wavelength, i.e., $c = 0$, which gives $I = I_o$ when the light passes through the reference cell.

The differential absorption spectroscopic technique has been used for many years. Early instruments used filters to select the light wavelengths. Current methods applied to discriminate between wavelengths include:

1. Optical filters
2. Diffraction gratings and photo-diode arrays
3. Diffraction grating and moving slits
4. Diode lasers

These different techniques are illustrated in Figure 3-13.

Numerous optical filtering instruments operating in the infrared region of the spectrum have been developed for the measurement of gases such as CO, CO_2, and the criteria pollutants, using "Luft" type or "microflow" detectors. These detectors monitor pressure changes due to differential absorption of light by molecules contained in the detector cell (Jahnke, 1993).

An optical filtering instrument using a photoacoustic detector, developed for ambient and industrial applications, has been used in conjunction with dilution systems to monitor organic compounds (Sollid, 1996). This detector monitors acoustic waves resulting from absorption of light by molecules directly in the sample cell.

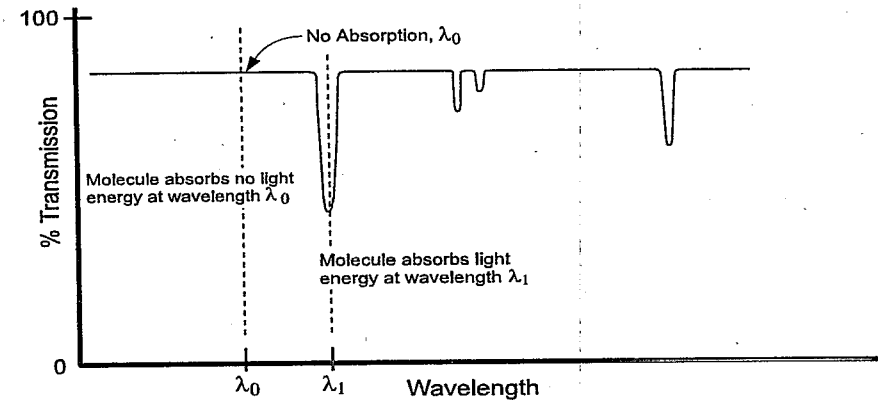

Figure 3-12. Transmission spectrum - example illustrating the differential absorption technique.

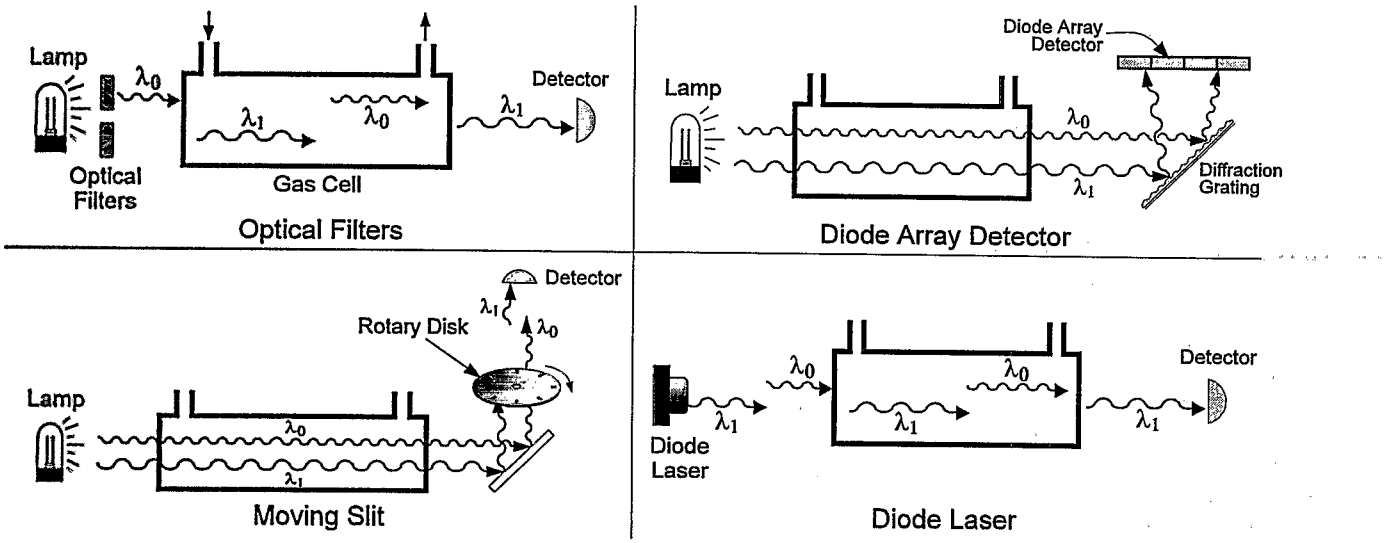

Figure 3-13. Differential optical absorption techniques.

A recently commercialized technique applied in the UV region of the spectrum employs a diode array detector to discriminate between the different wavelengths (Biermann, 1990). A diffraction grating is used to disperse the different wavelengths of the light source, and signals received from different segments of the detector are used to determine the transmittance. Moving slits, or slits on a rotating disc can be used to scan the spectrum of light dispersed by a diffraction grating. The moving slit selectively allows light of different wavelengths to reach the detector to determine the transmittance. The method has been applied to measure criteria pollutants, ammonia, mercury vapor, and some organic compounds. The newest commercialized application of the differential absorption technique employs diode lasers to measure HF and ammonia. By changing the temperature of a diode laser, it can be made to emit light at different wavelengths. Typically, the diode is attached to a Peltier cooler, and by changing the temperature by a few millidegrees, one can shift the wavelength from λ to λ_o. The transmittance can then be determined from the detector intensities as the laser light alternates between absorbing and non-absorbing wavelengths. The close-coupled sampling system used in conjunction with this analyzer is shown in Figure 3-5.

Differential absorption techniques applied in the UV-visible region of the spectrum can be used to measure halogens such as Cl_2 and F_2; aromatic compounds such as benzene, xylene, and toluene; carbonyl compounds such as acetaldehyde; and inorganic compound such as ammonia, chlorine dioxide, hydrogen sulfide, and nitric acid, and carbonyl chloride (phosgene). Although all of these gases can be analyzed by the differential absorption technique, only a few, such as ammonia, HF, and hydrogen sulfide, have had commercial instruments developed for their measurement.

A commercial instrument must be optimized for the compound being measured. The proper wavelengths must be selected to minimize the effects of interferences; calibration methods must be developed; appropriate filters, lasers, or detectors must be selected or developed, and the appropriate sampling interface must be selected to avoid loss of sample and provide for the proper instrument sensitivity. This process requires a program of research and development on the part of the instrument manufacturer that may require considerable capital investment. However, the market for non-criteria pollutant monitors is small and, in general, does not justify costs for optimizing a single-species monitor. The technology is available for developing needed instrumentation, but the incentive is often not sufficient to warrant investment in the development.

FTIR Spectroscopy. The FTIR spectroscopic method is a dispersive technique where an absorption spectrum over a limited spectral range is obtained for all infrared light absorbing compounds contained in the sample. Most commercially available FTIR analyzers operate in the mid-IR region (400 cm^{-1} ~ 4000 cm^{-1}). The technique allows for the measurement of more

than one gas species at the same time and is sufficiently general that it can be used at a wide variety of sources. For these reasons, the technique has generated interest for a number of non-criteria pollutant monitoring applications.

With the advent of compact and powerful microprocessors, the computation demands of such methods as mass spectrometry and Fourier transform infrared spectroscopy can be handled easily in lower-cost field instrumentation. Significant advances have been made in such instrumentation since the early 1990's to the point where the continuous measurement of hazardous air pollutants has become practical.

In the method, infrared radiation typically is directed through a sample cell as in the simplest of non-dispersive infrared spectrometers. In contrast to using an optical filter or a laser to transmit light at a specific wavelength through the cell, the FTIR source transmits light over a broad range of wavelengths. The IR radiation is modulated with an interferometer before the light enters the sample, that is, the light energy at each wavelength is varied from zero to some maximum value by using a mirror that moves over a small distance, x (in FTIR systems, a laser is used to monitor the mirror position). This all results in generating an "interferogram" (an interference spectrum) that shows the net intensity of the absorbed radiation at the detector, versus the mirror position, x. The interferogram contains much information, but not in a particularly usable form. The system microprocessor applies a mathematical technique called the "Fourier transform" to recalculate the detector intensity as a function of wavelength instead of as a function of the mirror position x. This is what is desired, a complete absorption spectrum over the wavelength region of the spectrometer.

Once the dispersed absorption spectrum information is obtained, the analyzer microprocessor must then extract both the qualitative and quantitative information desired. To do this, "library spectra" of the compounds being measured must be stored in the computer and referenced against the test data. The library spectra are obtained by analyzing samples of the compounds at known concentrations with the FTIR spectrometer. Various mathematical techniques are used in this process to obtain concentrations in parts per million.

The FTIR technique involves the application of numerous technical and mathematical tricks, however, its operation can be summarized simply as follows:

IR light is emitted over a broad spectral range

↓

Mirror moving over distance x, modulates light

↓

Modulated IR light is absorbed by molecules in the sample cell to create "interferogram"

↓

Interferogram converted by Fourier transform to absorption spectrum

↓

Library spectrum matched to test data to give concentration in ppm for each compound being measured.

The method can be relatively straightforward if the compounds in the sample do not absorb light in the same wavelength regions, i.e., if their spectral "fingerprints" are not similar. If these fingerprints are similar, or overlap, the method becomes more difficult to apply. This is the case when the sample contains hydrocarbons or other organic compounds of similar structure. Also, because water and/or carbon dioxide are often present in the sample at percent levels, discriminating between the spectral absorption of organic compounds at ppm levels within the broad spectral absorption regions of these two gases becomes more difficult.

The attraction of the FTIR technique is that it is a multi-component technique and reference spectra can be used for calibration. This does not mean that the FTIR technique does not have to be optimized for a given application. Each new use of the instrument requires the incorporation of library spectra of the compounds of interest over the range of concentrations expected at the source. Suitable reference spectra may have been generated by the analyzer manufacturer for similar applications, or they may be obtained from the EPA Emission Measurement Center (EMC) library or commercial FTIR libraries. If appropriate reference spectra have not been generated, individual spectra of the target gases at known concentrations and specific temperatures and pressures must be obtained.

The major differences between FTIR systems marketed for environmental applications are in the design of the optical bench used to create the interferogram. A major design goal for the moving mirror is to make it vibration insensitive for field use, and such designs as sliding wedges or flexing parallelogram arrange-

ments have been developed to meet this objective. A competing design goal relates to the distance that the mirror moves. The greater the distance, the greater the special resolution of the instrument. Other differences between instrumentation rest in the mathematical techniques used to extract the concentration data from the interferogram Fourier transform generated spectrum.

One of the more important decision-making factors associated with the FTIR technique is whether it has been applied successfully at a similar source for measuring similar compounds. With its increasing popularity, increasing numbers of reports are being published of successful applications. Examples have been given for monitoring criteria pollutants at coal-fired electric utilities (Dunder, 1994), solvent emissions at industrial coating facilities (Ayer, 1996, Bartak, 1996, Stock, 1996), for monitoring formaldehyde, methanol, phenol, and carbonyl sulfide (Kinner, 1995, Geyer, 1996), cyclohexane, ammonia, formaldehyde, methanol, carbon monoxide, methane at a high temperature, high moisture source (Reagen, 1996), hydrochloric, hydrobromic, and hydrofluoric acids at municipal waste incinerators and HCl at industrial process plants (Vidrine, 1993). Numerous other examples are given in the literature.

3.1.3.4 Ion-mobility Spectrometry

Ion-mobility spectrometry is a technique similar to the time-of-flight technique used in mass spectroscopy, except that the analyzer operates at ambient pressure and the ions drift to the detector in an electric field. Commercial ion-mobility instruments are single component instruments and have been optimized for the measurement of HF, HCl, NH_3, hydrogen peroxide (H_2O_2), hydrocyanic acid (HCN), Cl_2, and chlorine dioxide (ClO_2). A wide range of other gases, such as aldehydes, ketones, amines, polyaromatics, etc., are said to be measurable by this technique (Bacon, 1993). However, specific instruments for these gases have not been advertised commercially for source monitoring applications.

In this method, a radioactive source ionizes the molecules, which then drift through an electric field to an electrometer (Figure 3-14). The mobility (drift velocity/electric field strength) of the ions through the field is dependent upon the charge, mass, and shape of the molecule. An electronic shutter grid is used as a "gate" to periodically allow ions to enter the drift space. Smaller ions have a greater drift velocity than the larger ions and reach the electrometer earlier. The resultant instrument signal, showing the different ion signals as a function of time, appears much like a chromatogram and could be called an "ionogram." Concentrations are determined from the peak heights.

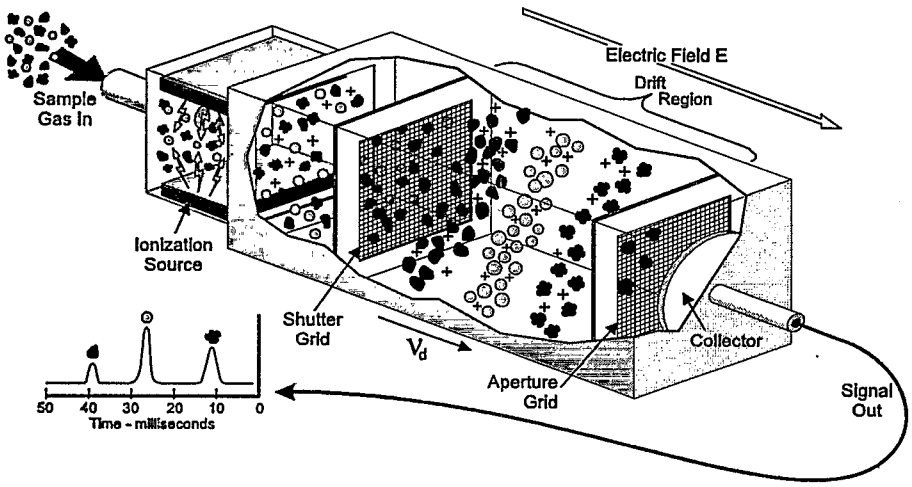

Figure 3-14. Ion-mobility spectrometer.

The ion mobility spectrometer does have some problems in discriminating between different compounds. These interference problems are resolved by several stratagems: 1) introducing chemicals ("dopants") into the gas stream to inhibit the ionization of interfering compounds, 2) using a permeation membrane to exclude or retard interfering compounds, 3) changing the electric field polarity to select positive or negative ions at the detector, or 4) scrubbing out interfering compounds before they enter the spectrometer. The research necessary to optimize the technique for specific compounds has limited the application of the method.

A related method to ion-mobility spectrometry is field-ion spectrometry. In this method, molecules are ionized by a radioactive source or are photoionized using a UV lamp. The method uses an oscillating electric field to neutralize interfering ions and allow ions of interest to pass through the drift tube to the electrometer. Field-ion spectrometry is said to be able to measure a wide range of organic compounds at part per billion levels; however, the method has been introduced only recently and is just becoming commercialized (MSA, 1996).

3.2 Monitoring Systems for Particulate Matter

3.2.1 Sampling Problems for Particulate Matter

Continuous monitoring of particulate matter emissions presents special sampling problems that are not encountered in the measurement of gaseous pollutants. These include resolving problems associated with 1) particulate stratification, 2) wet gas streams, and 3) particle deposition in extractive sampling systems.

3.2.1.1 Particulate Stratification

Particulate matter stratification across a stack or duct cross-section, including both variation in mass concentration and variation in particle size distribution, occurs in many instances and must be considered in the development of a particulate monitoring program. The extent of these effects are dependent upon the source application and the type of monitoring equipment that is used to sense the particulate concentration. In addition, effluent flow rate stratification is also likely to occur at most sampling locations and this may complicate the measurement of particulate matter mass emission rates.

Particulate matter stratification is due to the influence of inertial and viscous forces acting on the particles as they move with the gases through the effluent pathway. The significance of these forces is dependent on the flow stream characteristics and the specific bends, turns, flow obstructions, and length of the effluent ducts between flow obstructions. In the simplest terms, the particles within the effluent stream have much greater mass than the gas molecules and are thus subject to much larger inertial forces where changes in direction of the flow stream occur. Obviously, the extent of these forces depend on the size and density of the particles.

Where inertial forces cause particles to move in a direction different than the gas velocity, viscous forces are also exerted on the particles. These forces are dependent on the relative velocity between the particle and the gas stream and the aerodynamic size and mass of the particles. As a rough rule of thumb for industrial emission air flows, particles having a diameter smaller than 1 μm can be assumed to behave much like a gas and particles having a diameter 10 μm or larger are expected to exhibit substantial inertial behavior. Stratification across the flow stream is expected for 1 to 10 μm particles. The particle size distribution depends on the type of industrial process and the type and efficiency of control equipment that is installed.

Taken together, the above factors create particulate matter stratification at the majority of monitoring locations. To estimate or forecast the specific impact of these factors is infeasible based on theoretical models. To characterize the stratification profile would require obtaining particulate concentration data at many points in the duct. This would be very difficult and cost prohibitive. Furthermore, stratification profiles are likely to change 1) with varying flow rates corresponding to process rate changes, and 2) over time as a result of variations in control equipment performance, process operation, and fuel or raw materials. Decisions regarding monitor location can not be based on exact knowledge of the particulate matter stratification profile but instead must be based on an understanding of basic principles and the use of limited measurement data to make an informed choice. Ultimately, the acceptability of a particulate matter monitoring location is determined when the monitoring measurements are correlated with the results of manual gravimetric measurements. A non-representative monitoring location will not correlate well with manual test results that are obtained by traversing the entire duct cross section (see Chapter 7).

The effects of particulate matter stratification on duct concentration measurements cannot be completely eliminated. However, the effects can be minimized by selection of an appropriate measurement tech-

nique and selection of a measurement location and measurement point or path that will maximize the opportunity to acquire representative samples.

For sampling locations downstream of high efficiency control devices, very low particulate concentrations are expected except during malfunctions or certain periods of start-up or shut down when the control device must be bypassed. In most cases where high efficiency control devices are used, or where a stringent particulate matter standard must be met, control of large particles is reasonably assured and the remaining particle size distribution contains mostly small particles. In such cases, the effects of stratification are minimized since the small particles behave much like gas molecules and a representative sample can be obtained following simple principles described below.

Where higher particulate matter concentrations and larger particles are encountered, greater attention to selecting the measurement location and measurement points is warranted. Selection of a measurement location in a long straight run of duct or as far from flow disturbances as possible is a good first step. Pitot tube traverses should be conducted to construct velocity profiles at various operating loads or process rates. If no basis for estimating the particle size distribution exists, measurements should be made at several points across the duct cross-section using cascade impactors or other in-situ particle sizing devices. The resulting particle size information may be useful both in selecting 1) the type of monitoring equipment and 2) the measurement point or path for the monitoring device.

Another approach to selecting a particulate sampling location relies on the use of the monitoring device. "Portable" transmissometers with slotted probes have been manufactured and can be used (within the physical limits of the probe length, duct wall thickness, and duct dimensions) to perform measurement at a number of locations across the duct. Some in-situ light scattering devices can vary the area or volume in which particulate matter is sensed by changing the angle between the light source and the detector. For single point extractive systems or point monitors, varying the insertion depth of the probe or making measurements in several sampling ports may be possible. When attempting to use any monitoring device to detect stratification, the effects of temporal variations that occur during the experiment must be minimized. Ideally, two instruments should be used, one remaining at a fixed reference point and the other moving to various traverse points. Where the use of two instruments is impractical, care must be taken to maintain steady source operating conditions and sampling must be performed for a sufficient period at each point to characterize the normal fluctuations in emissions over time at each process rate of interest.

Good practice in all cases would generally require that point monitoring systems be located within the central portion of the flow stream (i.e., away from duct walls to avoid boundary layer effects), and at a point of average velocity in the flow stream with the flow direction parallel to the duct or stack walls. Cross-stack optical path measurement devices should be oriented so that the beam passes through the stratification gradient rather than parallel to the gradient. Such an orientation is much less susceptible to non-representative sampling due to the influence of stratification. Orienting the monitor path so that the light beam is in the plane defined by an upstream bend is an example of this approach. Also, locating a cross-stack monitor so that the light beam passes through the central area of the stack or duct minimizes the effects of boundary layers and eddy flows near the walls. Requirements for locating opacity monitors and examples for commonly encountered duct configurations are found in Part 60, Appendix B, Performance Specification 1 (PS1) (USEPA, 1996) which represent a consistent approach based on "engineering judgment." These principles and the requirements of PS1 generally should be followed for path sampling devices in the absence of other applicable criteria (or information) for a particular application. However, the PS1 location criteria should be considered as only a guide. Actual measurement data or other specific information should be given greater credence.

3.2.1.2 Particulate Monitoring In Wet Stacks

Particulate monitoring downstream of wet scrubbers or process streams where water droplets are present at the monitoring location limits the selection of monitoring equipment and may require that additional steps be taken. Some particulate monitoring devices can not be used where liquid water droplets are present. For example, charge-contact (triboflow) devices cannot be used. Transmissometers or other optical devices can not distinguish between water droplets and other particles and therefore can not be used without additional modifications to the source or effluent pathway. In the United States, new source performance standards (40 CFR 60.13(I)(1) (USEPA, 1996b) and state regulations provide for opacity monitoring exemptions where liquid water are present downstream of control devices because of this interference. However, in Germany, France and other European countries, particulate monitoring in wet stacks is required (Peeler, 1996).

Several options are available for particulate monitoring in wet stacks. Single point extractive systems with heated probes are available from several manufacturers. An extractive light scattering device has been developed with sufficient heating capability to vaporize liquid droplets before they reach the heated measurement cell. This device has been evaluated and tested in Germany (VDI, 1989). Extractive beta gauge systems that also vaporize liquid droplets have been used widely in France for wet gas monitoring.

Alternative approaches that convey a slipstream of the effluent through a heated device to vaporize liquid and which then employ either transmissometers or light scattering analyzers have also been used in Germany and other countries. A heated bypass system has been used with transmissometers for particulate monitoring on refuse incinerators and power plants in Germany. These systems have been evaluated and approved by TÜV Rheinland (TÜV Rheinland, 1985).

A similar approach has been developed for use with light scattering instruments normally used as in-situ devices. In this case, the slipstream is extracted from the stack, heated to vaporize droplets in an electrically heated cyclone, and then passed through a small heated duct with an installed light scattering analyzer to facilitate the measurement. This system has been used in Germany for several years and has been shown to perform successfully in the United States at a hazardous waste incinerator having a saturated exhaust stream and low particulate matter concentrations (Joklik, 1995).

The above solutions to monitoring particulate matter in wet stacks still require that comparisons to manual gravimetric tests be performed to correlate the output of the instrument to mass concentration units. Special care is required in performing the manual test methods because most in-stack particulate filtration methods (e.g., Part 60, Method 17) (USEPA, 1996b) can not be used in the presence of water droplets without special precautions and heating to ensure that the filters are not exposed to droplets. When out-of stack filtration methods are used (e.g., Part 60, Method 5) the temperature of the filter should be maintained only slightly above the sample stream dew point.

3.2.1.3 Probe/Sample Line Deposition Problems

Deposition of particulate matter in the sample probe and sample lines is a concern for extractive particulate monitoring devices because particulate matter that is deposited in the probe or sample lines represents a low bias in the measurement results. As with stratification, large particles are the most likely to be affected by probe deposition.

The primary method used to minimize probe and sample line deposition is to maintain high transport velocities through the tubing. Because isokinetic sampling must be performed at the point of sample extraction, the transport velocities are somewhat limited. The internal tubing diameters may be minimized to increase the transport velocity provided that the vacuum is not too high to be overcome by the pump or aspirator and thus create non-isokinetic sampling conditions. Another method of minimizing deposition is to keep the probe and sample lines as short as possible by using a close-coupled system.

A supplier of beta gauge devices has included a probe closure valve at the sample nozzle to protect the measurement system by excluding effluent gases and particulate matter when the monitor is not in the sampling mode and to minimize the effects of particulate deposition in the sample probe. The measurement system is operated for a discreet period to obtain a suitable amount of material on the paper tape. At the end of each of these batch sampling periods, the probe closure valve is shut briefly, creating a vacuum in the sample probe. Then it is opened quickly resulting in a pressure pulse of gas traveling through the probe to re-entrain particles that may have been deposited in the probe and transport lines.

The extent of particulate deposition problems for a specific system can be determined by periodically cleaning the probe and sample lines upstream of the analyzer. If a significant amount of material is found, then the maintenance interval should be shortened and greater cause for concern is warranted.

3.2.2 Continuous Particulate Monitoring

3.2.2.1 Perspectives for Continuous Particulate Mass Monitoring

No U.S. Federal requirements exist for the continuous measurement of particulate mass, although one is being proposed for sources that incinerate hazardous wastes (EPA, 1996). A few states have required continuous mass measurement systems through operating permits or through negotiated agreements; however, these applications have not been extensive. Continuous mass measurement requirements are common in Europe, particularly in the Federal Republic of Germany where both the regulatory and technical sophistication of continuous mass measurement has become quite advanced (Peeler, 1996).

missometer measures the ability of a flue gas to transmit light. A light scattering instrument measures the light intensity scattered by the flue gas particles. A beta gauge measures the transmission of electrons through a spot of collected particulate matter. All of these commercially available continuous mass monitoring instruments produce an instrument output that is something other than "grams per cubic meter" (or lbs/ft^3). This output, however, can be correlated to the particulate concentration. To continuously measure particulate mass, one first chooses an instrument that measures some property of the particles in the flue gas. The instrument readings are correlated with manual particulate source test method data from a manual reference method. Source and control equipment operating conditions are varied to obtain a range of particulate concentrations. A graph, or other correlation, is then made between the instrument response and the manually determined particulate concentrations.

This correlation results in an "analytic function" that relates the two techniques. The method defines how a statistical correlation is to be made and defines the acceptance criteria for the correlation. The principal concern in obtaining a valid instrument-manual method correlation is to make sure that the procedures are conducted in a representative manner.

1. Comparative measurements should be made at several source operating conditions to obtain a data spread suitable for establishing the correlation.

2. The automated system should measure a sample that is representative of emissions to the atmosphere.

3. The manual sampling method should extract a sample representative of that measured by the instrument system.

4. Measurements should be representative in time. Instrumental and manual measurements should be concurrent. Source operating conditions should remain stable during these measurement periods.

The correlation technique is valid only so long as the conditions under which a correlation was developed are representative of the source operation. Changes in operation that lead to significant changes in particle characteristics or the particle size distribution may affect the slope of the correlation line greatly. Changes in fuel, changes in control equipment, or changes in process operation may contribute to this problem. A new correlation should be developed in such situations.

Standards for continuous mass monitoring systems are used today in the Federal Republic of Germany (VDI, 1980 and FRG, 1992). A more general set of standards has also been prepared by the International Standards Organization (ISO) (ISO, 1995). A variation of the ISO 10155 method has been proposed as Performance Specification 11A for continuous particulate monitoring in the proposed hazardous waste combustor rule (USEPA, 1996). These methods are discussed further in Chapter 7 of this manual.

3.2.2.2 Measurement Techniques

Measurement techniques used in continuous particulate monitor systems are given in Table 3-1.

Of these methods, the light attenuation technique using transmissometers has been the most extensively studied. Extinction-mass correlation methods are used routinely in Germany and occasionally in the U.S. The light scattering and beta gauge techniques are being applied increasingly due to the good correlations that can be obtained.

3.2.2.2.1 Optical - Light Attenuation (Transmissometers). In a transmissometer, the light attenuation or transmittance through the flue gas is determined by passing a light beam across the stack interior. The intensity of the light returning, I, is compared with a previously determined reference signal, I_o, to give the transmittance, $T = I/I_o$.

A transmissometer may be constructed in two ways, using either a single pass system or a double pass system. In a single-pass system, the light crosses the stack directly to a detector. In a double-pass system (Figure 3-6), the light crosses the stack twice. The transceiver assembly on the left houses both the light source and light detector. By reflecting the projected light from a mirror located outside of the transceiver window, systems can be designed easily to check all of the electronic circuitry, including the lamp and photodetector, as part of the operating procedure. Most transmissometer systems include some type of air purging system or blower to keep the optical windows clean.

The way in which a transmissometer is used can affect its design. If the transmissometer data are to be correlated with particulate mass, red or infrared light may be more appropriate than using visible light as in opacity monitors. The smaller particles (<5 μm in diameter) contribute greatly to the opacity but not

Table 3-1. Automated Measurement Methods for Particulate Matter

Physical Basis	Technique
Optical	Light Attentuation (Transmissiometers) Light Scattering
Nuclear	Beta Ray Attenuation
Electrical	Contact Charge Transfer
Electromechanical (Loaded Oscillator)	Piezoelectricity Cantilevered Beam

to the particulate mass loading of the flue gas. Red light is not as sensitive to the small particles as it is to the larger particles, and thus gives a better correlation to particulate mass (Uthe, 1980). As discussed above, this correlation is done with respect to manual methods such as EPA Method 5 or 17 test data. Since the light transmittance, T, is reduced exponentially by an increase in mass concentration, a semilog plot of light transmittance versus concentration should yield a straight line, or linear correlation. Another method of developing the correlation is to first convert the transmittance data to optical density, where optical density, D, is defined as:

$$D = \log(1/T) \qquad \text{Equation 3-1}$$

Another expression that is used frequently for such correlations is "extinction," a parameter that normalizes the path length:

$$b = 2.303D/l \qquad \text{Equation 3-2}$$

where b = extinction
D = optical density
l = light path length

A graphical plot of either optical density or extinction against the manually determined particulate concentration should give a straight line correlation. The measurement sensitivity of this technique is approximately 10 mg/m^3 for a one meter optical path.

Extinction-mass correlations have been developed successfully for many types of emission sources. However, as implied above, correlations may be sensitive to changes in the particle-size distribution in the flue gas. In a practical sense, transmissometers used to provide mass measurements in Germany with retesting every 3 to 5 years have been found to maintain the original correlation (Peeler, 1996).

3.2.2.2.2 Optical - Light Scattering. When light is directed toward a particle, the particle may both absorb and scatter the light. If the wavelength of the light is large with respect to the size of the particle, a type of scattering called "Rayleigh" scattering occurs. If the wavelength of the light is approximately the same as the radius of the particle, a type of scattering called "Mie" scattering will occur (originally described by Gustav Mie in 1908). This form of scattering is shown in Figure 3-15.

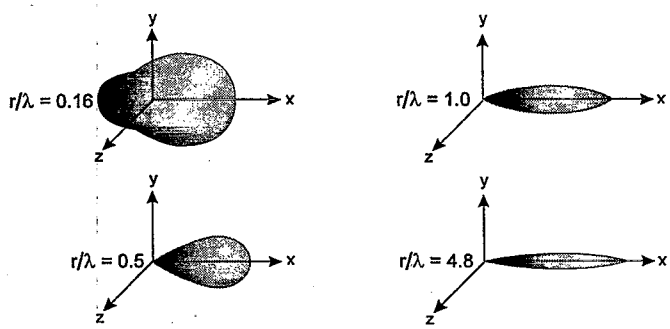

Figure 3-15. Angular dependence of the intensity of light scattered by a spherical particle with index of refraction 1.20. The intensity is arbitrarily normalized in each case. (Source: Ashley, L.E., 1958)

Note from the figure that for values of r/λ less than 0.5 (where r is the particle radius and λ the wavelength of the light), the particle will scatter the light in many directions - forward, backwards, up, down, etc. For values of r/λ > 1.0, the scattering will occur principally in the forward direction.

Baghouses and electrostatic precipitators used to control the emission of particulate matter will collect particles that are greater than 1 μm (1000 nm) in diameter effectively. However, collecting particles in the submicron range (<1 μm) is more difficult. These are the particles that will have a higher probability of escaping into the atmosphere. Visible light

(range 400 nm to 700 nm) scattering from these particles is, therefore, within the region of applicability of Mie theory for visible and infrared light.

Analyzers have been developed to take advantage of scattering effects. They can be designed to measure either back-scattered light, forward scattered light, or light scattered toward the side, at a specified angle. A side-scattering instrument is illustrated in Figure 3-16.

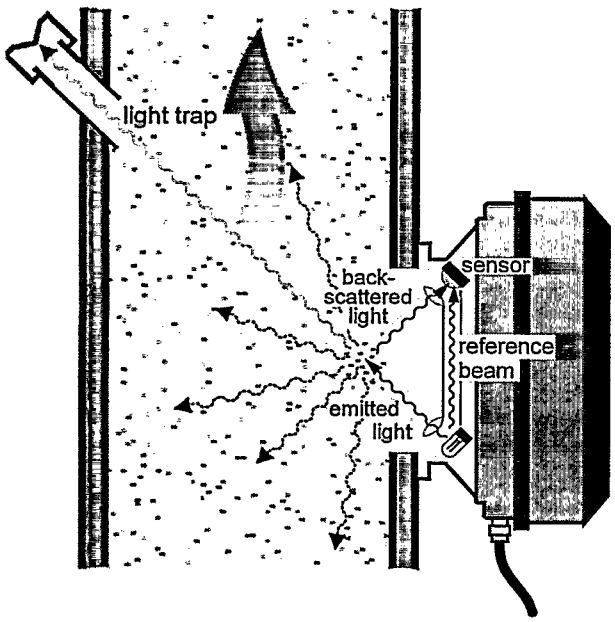

Figure 3-16. A Side-scattering continuous mass emission monitor.

In this side-scattering device, infrared light is focused on a sample volume. Instead of measuring the back-scattered radiation, the device locates a sensor above the lamp such that side-scattered light is detected. A reference measurement is made by monitoring the lamp intensity through a tube passing from the lamp to the detector.

3.2.2.2.3 Nuclear - Beta Ray Attenuation. When beta rays pass through a material, they can be absorbed or reflected by that material. The transmission of the beta rays is therefore attenuated and the reduction in beam intensity can be correlated to the amount of material present. By using a radioisotope for the beta source (e.g. Kr^{85}, C^{14}), "beta gauges" have been developed that can monitor particulate mass continuously (Figure 3-17) (Nader, 1975). In this device, the flue gas is drawn isokinetically through a probe. The sample may then be diluted to reduce the dew point to levels where condensation of flue gas moisture will not occur in the instrument. The gas is filtered through a glass fiber filter to produce a spot of collected particulate matter, which is moved between the beta source and detector for a determination of the beta ray attenuation. In practice, a moving filter tape allows the intermittent collection and measurement of one data point to produce a semi-continuous measurement.

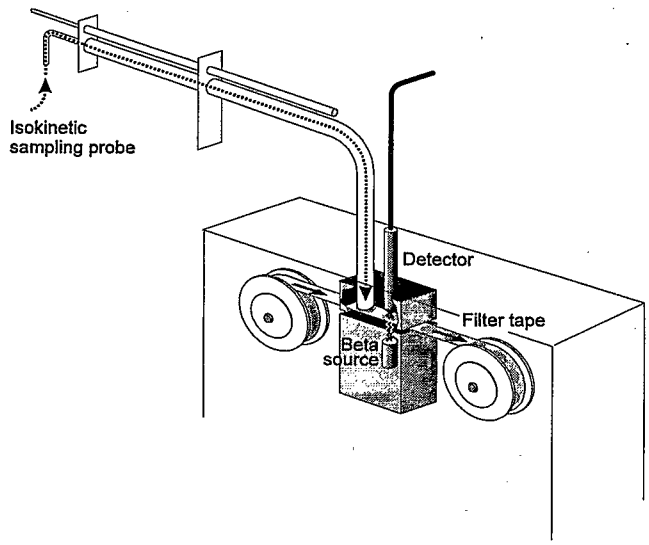

Figure 3-17. Typical beta gauge paper tape monitor.

The reduction of the beta ray beam intensity through the spot depends upon the electron density of the collected material and the amount of material present. To produce consistent measurements, a constant relationship must exist between the number of electrons per molecule and the molecular weight. This ratio is essentially the same for most particulate matter found in coal and oil combustion sources. In this method, the sample gas volume is controlled to provide a value for the particulate matter concentration. The range of the instrument is typically from 2 to 4,000 mg/m^3.

The method does require that the sample be collected isokinetically. Problems may occur with particulate deposition in the sample probe and sampling lines. As discussed earlier, strategies have been devised to minimize such deposition. Spot collection efficiency, particle composition, and gas volumes and dilution ratios are all factors that may produce error.

These problems may be minimized in some applications by first diluting the sample, using high transport velocities, or pulsating flow (Farthing, 1996).

3.2.2.2.4 Electrical - Contact Charge Transfer. When two dissimilar materials make contact, a net transfer of electrons from one material to the other can occur. This is not an effect based on the accumulation or transfer of static charges, but an effect based upon the intrinsic electronic properties of the materials themselves. The amount of charge transferred depends on the particle's work function, resistivity, dielectric constant, and the physical conditions of contact (particle deformation, duration of contact, area of contact, etc.) (Wang, 1988). The operating mechanism has been advertised as the "tribo-electric effect," a term which is not commonly found in the scientific literature. This has tended to confuse the evaluation of the technique.

The instrument is simple, consisting of a metal surface probe inserted into the stack. It has been qualitatively successful as a bag-house particulate alarm monitor. The instrument, however, lacks a method of probe calibration and has shown problems for monitoring after electrostatic precipitators because of static electrical charges on the particles. Also, small particles may follow the gas streamlines around the probe and never make contact for the measurement.

3.2.2.2.5 Electromechanical - Piezoelectricity, Loaded Beam. Electromechanical devices have been developed on the principle that the frequency of a vibrating oscillator will change if the mass of the vibrating element changes. A piezoelectric crystal, a cantilevered beam, or oscillating metal band may be used to provide the mechanical vibration. When particulate matter comes into contact with the vibrating element, it adheres to it and changes its total mass, and consequently, its vibration frequency. This mass-dependent vibration frequency is then measured as the correlation parameter.

When applied to flue gas measurements, the sample must be withdrawn isokinetically from the flue and it must be diluted to avoid condensation of the flue gas moisture. When the particles don't adhere to the vibrating element, the data are not representative. When the particles do adhere, the vibrating element eventually will become overloaded and it must be cleaned and recalibrated. Although some interest in this method has been shown, it has not become commercially available technology.

3.2.2.2.6 Other Methods. Several newer methods for continuous particulate monitoring have appeared on the commercial market. In what is termed an "acoustic energy" technique, particles impacting on a probe produce acoustic waves in the probe transducer. The oscillations produced are used to count the impact of single particles on the probe and thus provide a relationship to the flue gas particulate matter concentration.

In another technique, variation on transmissometry utilizes fluctuations in the light transmission due to the flue gas particles passing through the light beam. This generates an instrument response that is directly proportional to the particulate concentration.

3.2.2.3 Choosing a Continuous Particulate Monitoring System

Numerous technical issues are involved in choosing a continuous particulate monitoring system. First, the flue gas stream must be well characterized to determine the presence or absence of water droplets, particulate concentration levels, and the degree of particulate stratification. A selection process that considers these issues is illustrated in Figure 3-18.

3.3 Monitoring for Metals

3.3.1 Sampling Problems for Metals

Either extractive or in-situ sampling methods can be used for monitoring metals. However, measurement problems develop when a metal is present in the flue gas in both the vapor and solid phases. Mercury is a typical example, where most of the total mercury is present as a vapor, although some may be bound in the form of mercuric chloride or other compounds in the particulate matter. Simple optical instrumentation can detect the mercury vapor, but not the other mercury compounds. To obtain a value for total mercury, either an extractive technique must be employed to reduce these compounds for subsequent measurement, or the particles and vapor alike can be heated to extremely high temperatures (as in an electric arc, a plasma torch, or a focused high energy laser beam) to emit characteristic spectra.

In extractive metals monitoring systems, metal amalgamation and deposition in the probe and sampling lines present a significant problem. Here, close-coupled systems or very short sampling lines may be necessary to obtain reproducible results.

3.3.2 Mercury Monitoring Methods

Commercial systems are available for monitoring mercury on a continuous basis. Municipal incinerator regulatory requirements in Germany and other European countries have promoted the development of continuous monitoring methods. In the United States, mercury monitoring requirements and mercury CEM performance specifications have been proposed for facilities that incinerate hazardous waste (61 FR 17358) (USEPA, 1996).

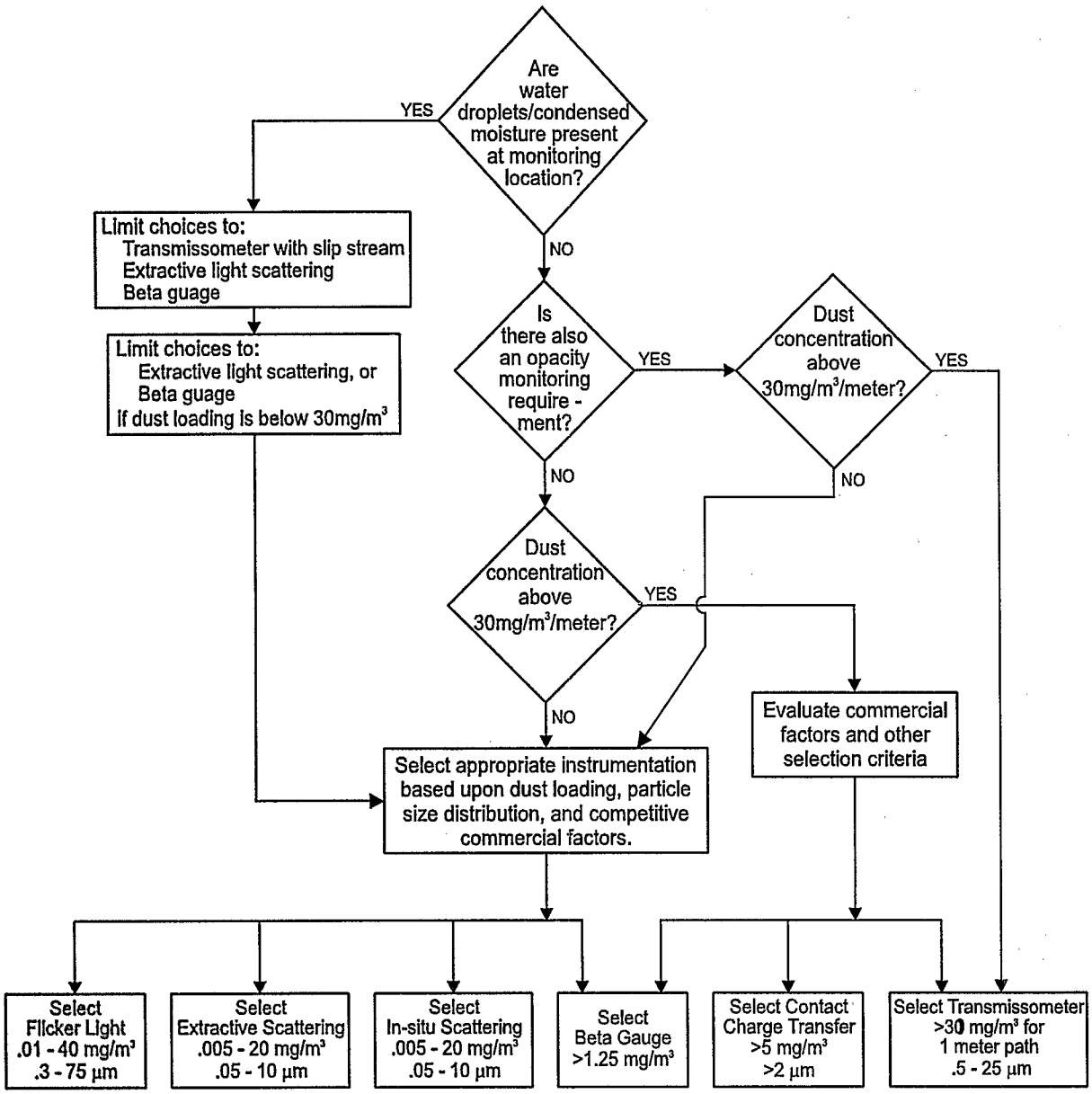

Figure 3-18. Selection process for particulate monitors.

In most mercury monitoring methods, mercury vapor is analyzed by light in the ultraviolet region of the spectrum. The simplest method is to merely project a UV light into the stack as in an in-situ instrument and monitor the absorption of light by the elemental mercury vapor. However, if mercury is present in other molecular forms, such as mercuric chloride ($HgCl_2$), total mercury will not be measured. Although in many incineration facilities elemental mercury comprises greater than 90% of the total mercury emitted, interest remains to measure total mercury. As a result, various stratagems have been devised to reduce the mercury compounds to elemental mercury, vaporize the elemental mercury, and measure the vapor through UV light absorption techniques.

In one method, an isokinetically extracted continuous sample is heated in an infrared oven to volatilize particulate bound mercury and a sodium hydroboron

solution is used to reduce all mercury compounds to elemental mercury. Elemental mercury then is measured using a UV photometer. In another method, mercury compounds are reduced chemically using stannous chloride and the elemental mercury is amalgamated with gold, which then is heated to release the mercury as vapor to be measured using a UV photometer.

In a new microsensor technology, mercury vapor adsorbs on the surface of a thin noble-metal film. The electrical properties of the film change quantitatively to give a measurement of the amount of mercury present (Glaunsinger, 1995).

Although mercury monitoring methods are commercially available, to measure total mercury adsorbed or bound on particulate matter, a continuous isokinetic sample must be obtained and the sample reduced to elemental mercury. However, chemical systems and ovens used in the various system designs require frequent periodic maintenance. These maintenance demands are typically greater than for traditional criteria pollutant monitoring systems.

3.3.3 Multi-Metal Methods

Title III of 1990 Clean Air Act Amendments has listed ten other metals, in addition to mercury, that are to be regulated as hazardous air pollutants (air toxics). These metals are: antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), nickel (Ni), and selenium (Se). Whether these metals will be required to be monitored individually and continuously is unclear. Nevertheless, considerable interest exists in the development of instrumental methods for metals. (See, for example, Durham, 1995). As in the initial development of gas monitors, multi-metal methods are essentially laboratory techniques adapted for field use. The techniques of x-ray fluorescence spectroscopy and atomic emission spectroscopy have seen the most application. The atomic emission spectroscopic techniques differ by the manner in which the metal atoms are excited - either through the use of a laser, a radio-frequency plasma, or a microwave generated plasma.

3.3.3.1 X-Ray Fluorescence Spectroscopy

X-ray fluorescence spectrometry is being applied in a manner similar to that of the beta gauge used to continuously monitor particulate matter. To analyze for metals, particulate bound and gaseous metals are collected on an activated carbon impregnated filter. The collected material is then exposed to x-rays, which excite the atoms to higher electronic levels. As the excited atoms de-excite, they fluoresce, emitting light at wavelengths specific for each metal. The amount of emitted light is measured and the flue gas metal concentration calculated.

X-ray fluorescence spectroscopy is a well-established technology; however, the commercial continuous monitoring systems applying the technique have not been developed fully. Current systems involve collecting and analyzing the filter samples in a batch mode, not a continuous mode.

3.3.3.2 Atomic Emission Spectroscopic Systems

Atoms can be excited in many ways and when excited sufficiently, will emit light energy. Two excitation methods under development are that of inductively couple plasma and laser spark spectrometry.

3.3.3.2.1 Inductively Coupled Plasma Spectrometry. In this technique, a radio frequency generated plasma is used to heat the flue gas sample to temperatures greater than 10,000°C (Figure 3 -19).

The light emitted by the metal atoms excited at this extreme temperature is measured using a diffraction grating and photodetectors as shown in the figure. A system is under development (Seltzer, 1994) that extracts a sample continuously and isokinetically from the stack, which is then subjected to the heat of a plasma torch.

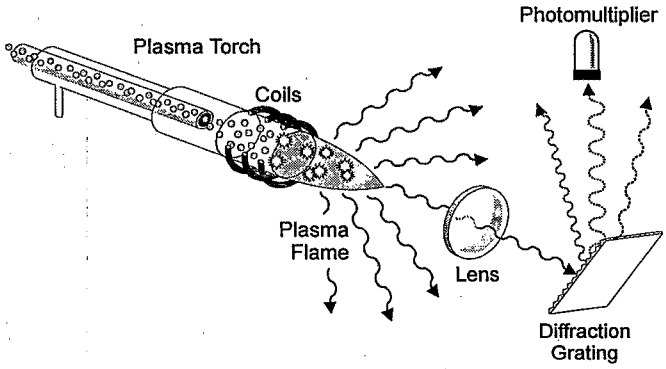

Figure 3-19. Inductively coupled plasma technique.

3.3.3.2.2 Laser Spark Spectrometry. In laser spark spectrometry, a high energy laser is used to excite metal atoms in the stack (Figure 3-20). Here, the laser provides energy to excite the metal atoms, both in the gaseous phase and those adhering to the surface of the particulate matter. The light emitted by the excited metal atoms is again collected and analyzed.

Validating multi-metal monitoring methods has proven difficult. Uncertainties associated with the manual

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Chapter 4
Alternatives to Monitoring Instrumentation

Alternatives to the installation of traditional CEM systems have been, and can be, used to monitor emissions. These alternatives are often applicable to sources where independent monitoring instrumentation may not be required to meet the goals of a regulatory program. To monitor process and control equipment performance, certain NSPS sources employ "parameters," such as pressure drop, temperature, or water injection rates (see Chapter 2, NSPS Parameter Monitoring Requirements and Table 2-3), instead of installing CEM systems. Similar provisions are included in other federal and state monitoring requirements. Sources regulated under the air toxics or the "enhanced monitoring" provisions of the 1990 Clean Air Act Amendments are likely to have the flexibility to consider such options.

Alternative monitoring options include: 1) using parameters as indicators of proper operation and maintenance practices, 2) using parameter values directly as surrogates for emissions determinations, 3) using parameters in models that calculate emissions, 4) performing mass balance calculations, or 5) employing a CEM system to monitor a more easily analyzed gas as a surrogate for one that is more difficult to analyze. Deciding whether to use an alternative method depends upon the application and how the data will be used. To assist in such decisions, the basic principles of these techniques as well as their advantages and limitations will be discussed in this chapter.

4.1 Parameter Monitoring

Parameter monitoring has been used in a variety of ways in regulatory programs. These are summarized in Figure 4-1.

Beginning with the original application of the monitoring process and control equipment performance, parameter monitoring has extended to providing a basis for the calculation of source emissions. Emission calculations have been performed since the original development of air pollution control equipment in the form of engineering design calculations (for example, see Mycock, 1995). Design engineers typically will attempt to determine equipment performance from operational parameters. In terms of air pollution control equipment, the question facing the engineer is, if I vary this parameter, or if I vary that parameter, will the pollutant emissions increase or decrease?

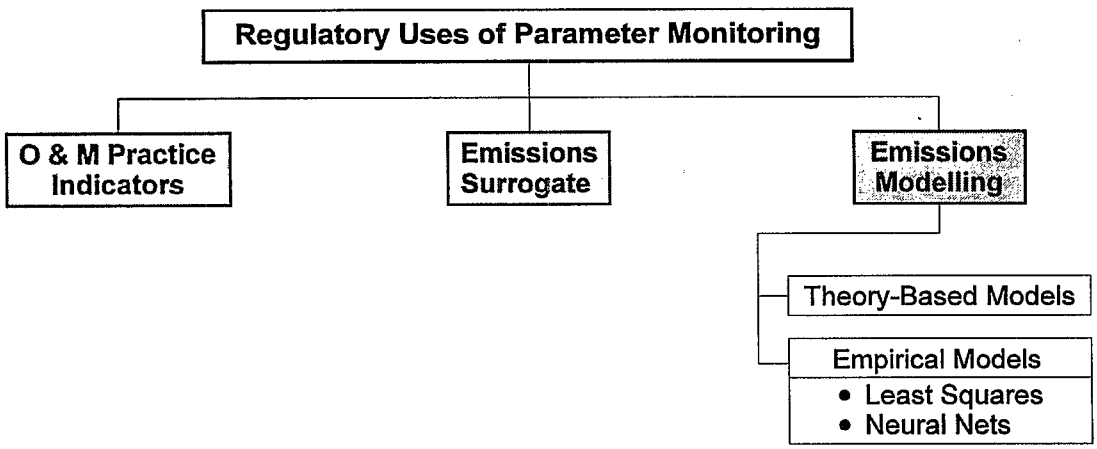

Figure 4-1. Uses of parameter monitoring in regulatory programs.

This question also has drawn the attention of regulatory agencies, and due to relationships between parameter values and emissions, has led to the reporting of parameter data to both federal and state agencies. The original regulatory use of parameter data and CEM data was to indicate whether process and control equipment were being operated properly. A continued record of unsatisfactory parameter data could result in a notice and finding of violation of operation and maintenance requirements. A subsequent requirement to perform a source test for determining compliance with an emission standard might also result.

A more direct application of parameter data is to use it as a surrogate for emissions. Rather than requiring the determination of emissions by CEM systems or a manual method, a surrogate parameter level is established which is correlated to the emissions standard. An exceedance of this parameter level could then be used for enforcement and a source test may not be necessary (depending upon the applicable regulation or permit requirements).

An extension of the use of parameter data is to "predict" the performance of the process or control equipment from the parameter data. If the process is well understood, first principle (i.e, theoretical or phenomenological) calculations may be performed. Another technique is to "correlate" parameter data to emissions data. An initial study is performed by varying and monitoring process and control equipment parameters while monitoring emissions using reference methods or CEM systems. One can then correlate the data to develop a statistical model that can "predict" emissions.

Both theoretical and statistical emission models based on process and control parameter inputs are used today to meet emission monitoring requirements. A number of states have accepted their use, and the federal proposals addressing the 1990 Clean Air Act enhanced monitoring requirements have been receptive to their application (USEPA, 1993, Bivins, 1996).

The different uses of parameters, illustrated in Figure 4-1, provide a means for agencies to track control equipment performance and emissions without the application of CEM systems or performing source tests. Although in some cases the data may not be as accurate as that obtained from independent test methods, such levels of accuracy may not be necessary. For stable, nonfluctuating sources having low emissions relative to the compliance limit, data that can assure compliance with the standard may have a higher inaccuracy than that generally acceptable (e.g., >20% of the reference method or >10% of the standard), but may still be defensible. For example, if a stable source has a VOC emission limit of 50 ppm, but normally emits 5 ppm, even with 100% uncertainty (±5 ppm), one could still assume that the source is in compliance. However, the acceptability of such uncertainty depends on the use of the data. Moreover, this scenario may not be acceptable if the emission limit is 10 ppm or the data were to be used in a market trading program.

4.2 Parameters and Sensors

A parameter is a property whose value can characterize or determine the performance of process or control equipment. Such properties may be temperature, pressure drop, liquid to gas ratios, percent oxygen, or even the position of a damper.

The values of parameters are determined by "sensors." In the broadest sense, a sensor is "a device that receives and responds to a signal or stimulus (Fraden, 1993)." A thermocouple or resistance temperature device (RTD) may be used to measure temperature, a pressure transducer to measure pressure drop, flow monitors to measure liquid to gas ratio, an oxygen monitor sensor to measure percent oxygen, and a simple on-off switch to monitor the damper position. Sensors normally are assumed to be some mechanical, electrical, or chemical device that generates an electrical response, but human perception also can serve to determine parameter values. For example, the visible emissions observer performing EPA Method 9 is determining a value for the parameter, opacity, which may characterize the performance of a bag house or an electrostatic precipitator. Or, in an iron and steel plant (NSPS subpart AA), each shift operator may note the furnace static pressure, again a parameter.

In process and control equipment, sensors tend to be simple devices that generate an electrical response. They do not, in general, incorporate sophisticated linearization and calibration features such as those used in CEM systems. They are basically the stripped down version, the sensing elements incorporated in CEM systems. For example, the zirconium oxide electrocatalytic cells used in many CEM oxygen analyzers are the same type of cells used as "sensors" in automobiles for engine and emissions control.

4.3 Parameter Monitoring Used as an Indicator of Equipment Operation and Maintenance

As discussed in Chapter 2, plant operational parameters or control equipment parameters have been specified in the New Source Performance Standards for certain source categories. In these applications, the parameter data are intended to determine whether the process or control equipment is operating properly. Proper operation, in turn, means that the plant equipment is operating in a manner such that the emissions limits (standards) are most likely being met. In NSPS applications, parameter data may indicate possible problems in plant performance, but compliance with emission standards traditionally has been determined by source testing (or in some cases, CEM systems) under specified operating conditions.

The use of the parameter values varies depending upon the regulation. In the simplest case, a regulation merely may require that the parameter values be determined, such as in the NSPS requirements for monitoring the pressure drop across wet scrubbers used to control particulate emissions in the phosphate fertilizer industry, coal preparation plants, ammonium sulfate manufacture, etc. (CFR Subparts T, U, V, W, Y, and PP, respectively). No recording or reporting requirements are given for these examples, but the required permanent record can be used by the regulatory agency to assess plant operations and target problem facilities for follow-up actions.

State programs also have used parameter monitoring for determining the adequacy of plant operation and maintenance practices. Many programs include general provisions in state implementation plans requiring good engineering practice in the operation and maintenance of control equipment.

4.4 Parameter Monitoring Used as a Surrogate for Emissions

An extension to requirements for monitoring and recording operational parameters is to establish some trigger value for the parameter. Here, a parameter baseline or trigger value is established during a source test, where the source test is conducted to determine compliance with the emissions standard (lbs/hr, ppm, etc.). This trigger value then can be used in one of two ways: 1) it can trigger a reporting requirement, analogous to reporting excess emissions by sources with CEM systems, or 2) it can be used directly as a surrogate for an emission compliance limit.

4.4.1 Parameter Monitoring as a Surrogate for Reporting Excess Emissions

Parameter values can be used as surrogates for emission values to report problems in the operation and maintenance of emission control equipment. A typical regulatory statement for parameter monitoring for particulate control equipment is:

> "...report to the Administrator, on a semiannual basis, all measurements (pressure loss and water supply pressure) over any 3-hour period that average more than 10% below the average levels maintained during the most recent performance test in which the affected facility demonstrated compliance with the mass standards..." (40 CFR 60.143 Subpart N).

Here, one assumes that the facility is operating at or below its compliance value and that the parameter values reflect the operating conditions of the control device (usually a wet scrubber) at that level. If parameter levels fall within a range of acceptable values established during the compliance test, one assumes that the scrubber is continuing to operate in a manner where the facility is in compliance with the underlying emission limit. In this sense, the parameter value stands in as a surrogate for the emission compliance value.

Note, however, in the example given, that the trigger level is not at the parameter level determined during the compliance test, but at a level 10% lower. In a typical venturi scrubber, an increase in pressure drop increases the particulate removal efficiency of the scrubber. A decrease in the pressure drop means that less particulate matter will be removed. Since the sensor measurement accuracy may be ±5% and since some inaccuracies may have occurred in the source testing, the pressure drop is allowed to decrease by 10% from the baseline level before it is required to be reported. For even greater flexibility, some regulations allow a reduction of 30% before reporting is required (see for example, 40 CFR 60, Subpart HH, lime manufacturing plants).

Many other examples could be given of this use of parameters as surrogates for emissions. In Subpart GG, gas turbines using water injection to control NO_x emissions must report any one hour period where the water-to-fuel ratio falls below the value determined to demonstrate compliance. Incinerator temperatures in Subpart MM, RR, and other coatings operations are to be reported when they change from some specified compliance level.

If parameter values fall below such trigger levels, the agency may require the source to improve its operation and maintenance practices, or may require a compliance test be performed to determine if the source is meeting its emissions standards. Also, if sensors installed to monitor equipment performance are not operating properly, parameter data will no longer be useful and a compliance test again may become necessary.

4.4.2 Parameter Monitoring for Direct Compliance

A new approach appeared in a 1993 proposal for enhanced monitoring (EPA, 1993) where parameter monitoring was proposed as a method for determining directly the compliance of a source with emissions standards. In this approach, the source owner or operator would be required to "justify that a known and consistent relationship exists between the emissions subject to an applicable limitation or standard and the parameters being monitored." This is not much different from using parameters as a surrogate limit in excess emissions monitoring, as prescribed in certain NSPS requirements. The differences are that:

- The parameter level is used as a surrogate for the emissions standard.
- The source owner would be required to establish the parameter value or values that would assure that the source is in compliance with the emissions standard.

That established parameter value has been called the "demonstrated compliance parameter limit," or DCPL. Although the proposed enhanced monitoring rule was withdrawn in April 1995, the concept of the DCPL, the stand-in or surrogate emissions standard, still remains.

The question as to how parameter limits actually relate quantitatively to emission values depends on the underlying relationship, the accuracy and precision of the emission measurement method, averaging periods, and other factors. To answer this in practice, one must obtain further information by testing at different operational levels. One can correlate the parameter values with emissions over a narrow range of operating conditions to establish the DCPL. A typical performance curve for a venturi scrubber is given in Figure 4-2. Here, as the pressure drop across the venturi throat increases, the efficiency in removing particulate matter increases.

At some point on the curve, a pressure drop will correspond to the compliance value, the emissions standard for the facility. Some variability will exist in the testing procedures used to establish the correlation and in the accuracy of the sensor used to determine ΔP. This range of variability is shown by the confidence intervals in the figure. The agency may therefore not accept a 1:1 correlation between the emissions standard and the correlation, but establish the surrogate standard, P_{std}, at a higher value to account for the variability. If the pressure drop is maintained at the DCPL value or higher,

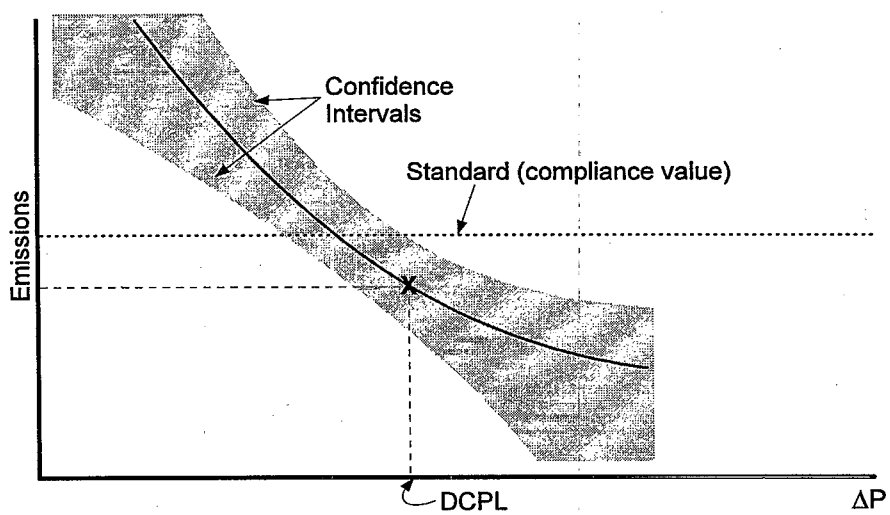

Figure 4-2. Operational parameters correlated to emissions. Establishing the demonstrated compliance parameter limit (DCPL).

some assurance exists that the emissions standard is being met, within the uncertainty of the correlation.

Many examples of using parametric monitoring to demonstrate compliance with emissions regulations have been published. Bills (Bills, 1995) describes applications in the pharmaceutical industry for thermal oxidation systems, condensers, and adsorption systems used to control VOC emissions. In these applications, direct measurements of multiple gaseous components in the process gas streams became overly complicated and resource intensive. Instead of using sophisticated monitoring instrumentation, simpler parameter monitoring approaches were adopted in exchange for accepting more stringent "worst case" DCPLs.

This use of parameter surrogates in place of using CEM systems to monitor emissions may appear straightforward. However, as in all emission monitoring techniques, the method is application dependent. In determining the appropriateness of the method, one should consider the following factors:

- The relationship between the parameter or parameters should be straightforward.
- The relationship should hold for all operating conditions.
- The correlation between emissions and the parameter should have a high degree of confidence with narrow confidence and tolerance intervals.

Parameter surrogates are most appropriate when the relationship is a simple one, such as in using incinerator temperature for VOC control, or water-to-fuel ratio for gas turbine NO_x control. For the method to be practical, no other operating variables should affect the correlation significantly. If they do, they should be included in the correlation, which will then make the correlation more complicated and more uncertain. These issues are discussed in detail by Evans (Evans, 1994).

The DCPL approach is similar to a predictive method since the DCPL value is established on past data or performance data to predict present compliance with emissions standards. It differs from the statistical predictive emission monitoring (PEM) models in that it is less refined (see Evans, 1994) and is established over a narrow range of operating conditions. In a DCPL approach, parameter values such as pressure drop, temperature, or supply pressure are reported to the agency. In a predictive method, emissions values calculated by the model from parameter values are reported to the agency.

4.5 Emission Modeling - Predictive Emissions Monitoring Systems

Many applications occur where parameter relationships to emissions are more complicated than establishing a simple DCPL and sensor determined parameters might be better incorporated into a predictive emission monitoring (PEM) model, or system. In the PEM model approach, emission values are calculated by the model from the input parameter values.

When developing a predictive model, parameter and emissions data are accumulated under various operating conditions. Then the data are used to develop the model. Two approaches are possible:

1) If the source or control equipment operation is well understood, first principles calculations can be made to determine the emissions. Based upon the physical and chemical effects of operating parameters on emissions, the actual emissions may be determined. This approach is often called the "first principles" or "phenomenological" approach.

2) If the effects of operating parameters on emissions are not well understood, or if theoretical calculations become too complicated, statistical methods may be applied. Linear and nonlinear regression techniques have been used successfully in many situations. Neural net methods also have become popular in these applications.

No one modeling approach can be said to be the "best." As with CEM systems, one must consider tradeoffs in each application. Both first principle and statistical models have passed relative accuracy tests in specific applications (Hung, 1994, Clapsaddle, 1995, Clapsaddle, 1996).

Predictive systems are basically empirical models. Even the first principle approaches use past data for evaluation purposes. The theory establishes the form and mathematical functions of the model, and test data commonly are used to introduce empirical constants to fine-tune the model. In building these models a test program must be developed that can provide representative emissions and parameter data over the probable, expected range of operating conditions of the emission source.

4.5.1 First Principle Models

Models can be developed from the fundamental theory associated with the operation of a process or a pollution control device. Depending on the process, principles of thermodynamics, chemical kinetics, fluid flow, and so on, may be applied. First principle models have been applied to calculate nitrogen oxide emissions for can-type gas turbines (Hung, 1993, 1994, 1995). Also, theoretical design equations have been developed for most types of air pollution control equipment: particulate scrubbers, gas absorbers, condensers, electrostatic precipitators, etc.

First principle models provide for an understanding of a process and the relative importance of the input parameters to its performance. A pure first principles model does not depend upon historical data and can be used over the full range of process operation.

4.5.1.1 Semi-empirical Models

Theoretical design equations can give good qualitative information, but quantitative information having the accuracy necessary to be legally enforceable usually is not obtainable without empirical correlation. Not all of the effects of process variables may be known and the values of the necessary input parameters may not be of sufficient accuracy to give correct results. The problem here is that most devices are too complex. Calculating emissions from first principles often requires too much information to be practical. For example, in the "infinite throat model" for Venturi particulate scrubbers a knowledge of the particle size and droplet size is necessary (Yung, 1977). In practice, one would have to integrate over the particle size distribution to obtain a realistic number. Unfortunately, the distribution of particle sizes in a flue gas is both difficult and expensive to determine accurately. The model may be good for design applications, but because of the requirement for accurate input data, is limited in practical applications for emissions calculations.

A compromise to this problem is to develop a semi-empirical model. In a Venturi scrubber example, the "contact power" theory (Calvert, 1972), the efficiency of the scrubber in removing particulate matter is related to the power required to move the process gas and liquid through the system. The exponential relation developed depends upon empirical constants determined by experiment. The net result is a model that incorporates some physical understanding of the process, but which is fine-tuned with experimental data --- the semi-empirical model.

Hung (Hung, 1993) has developed a semi-empirical model for annular (can) type gas turbines to calculate NO_x emissions. Based on operating conditions, ambient conditions, combustor geometry, and the type of fuel used, the model has been used to generate data comparable to that obtained from CEM systems. The strength of the model does depend upon the quality and amount of test data used in the semi-empirical correlation (Hung, 1994).

4.5.1.2 Mass Balance Calculations

A much simpler version of the theoretical approach is to calculate mass balances in the process. Theoretically, for an uncontrolled emissions source, "what goes in should go out." For fossil-fuel-fired boilers, sampling and analysis for sulfur in fuel has been allowed as an option to CEM systems for certain Part 60 and Part 75 sources regulated by EPA. Fuel analysis is particularly convenient for oil and gas fired boilers, where fuel flow rates are easily determined and the sulfur content is homogeneous. For coatings operations the emission of volatile organic compounds (VOCs) can be calculated from the VOC content of the coating (paint) and solvents and the amount of paint and solvent used. Mass transfer calculations have been used for estimating emissions in very small emission sources such as those found in electroplating operations and degreasers (Siebert, 1995).

Comparisons between mass balance calculations and CEM systems do not always come out as expected. When the plant operating engineer's mass balance calculations and the environmental engineer's CEM results do not agree, winning the argument may be less important than who is right, especially where emissions up the stack correspond to loss of product. In the case of heat rate calculations vs CEM systems, Cashin (Cashin, 1996) has addressed the many issues involved in such debates.

4.5.2 Empirical Modeling

When developing a model from physical, chemical, or engineering principles is not possible, a statistical approach may be applicable. Beginning with the effect of only one parameter on equipment performance, we could first assume a linear relationship between the parameter and emissions. That is, if a change occurs in the parameter x, the emissions y will change by a constant factor, b, according to:

$$y = a + bx$$

where a and b are the intercept and the slope, respectively, of the regression equation.

In practice, one desires a model that will be valid under a range of values of x. Thus, a number of tests would be conducted to obtain data that might appear as that shown in Figure 4-3.

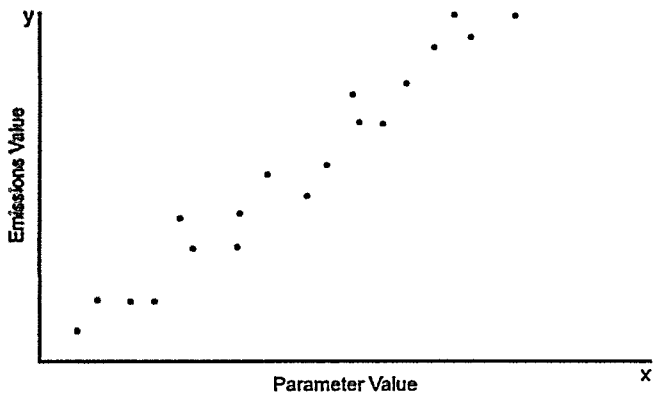

Figure 4-3. Test data. Emissions as a function of the parameter values, x.

Obviously scatter occurs in the emissions data. The scatter in y is due to uncertainties and variability in the emissions measurements because of problems in measurement, difficulties in keeping process variables (parameters) other than x constant during the testing, and to unknown variables that may be affecting the process.

In the statistical methods, the goal is to find an equation that best summarizes the test data and predicts emissions to within an acceptable level of confidence. Based upon the quality of the input data and the choice of parameter or parameters or, based on past data, how confident are we in our equation predicting future values?

Statistics can answer these questions for us and many statistical methods have been developed to fit curves to data and qualify the results. The least squares linear regression and multiple linear regression techniques are very useful in this regard. The extended statistical method of neural nets has also been useful in providing greater flexibility for nonlinear expressions.

4.5.2.1 Least Squares Linear Regression Techniques

The least squares technique is one of the simplest methods used to fit a line to emissions/parameter data. In the example above, if y is a linear function of the parameter x, the line $y = a + bx$ is such that if one takes the deviation from each point to the line and squares the deviations, the constants a and b in the equation will be such that the sum of the squares is the smallest possible value (Figure 4-4).

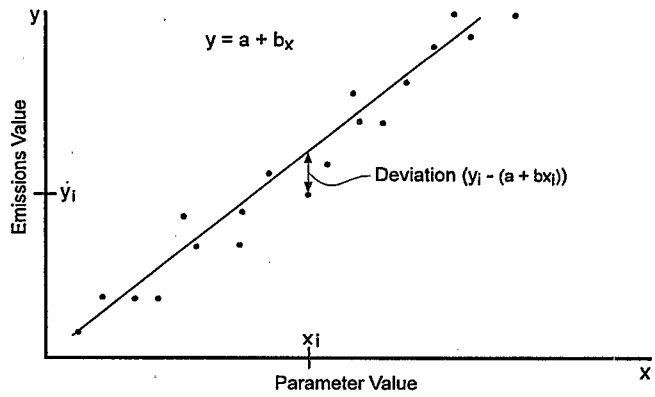

Figure 4-4. Linear regression of test data.

In mathematical terms a and b are calculated to be such that

$$\sum(y_i - (a + bx_i))^2 = \text{a minimum value}$$

One can show that the values for a and b which define the line of minimum deviation (the regression line), can be calculated from n data sets (x_i, y_i) as follows:

$$a = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{n\sum x_i^2 - (\sum x_i)^2}$$

$$b = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{n\sum x^2 - (\sum x_i)^2}$$

The calculations are tedious if performed manually, however. Computer programs are available to do such routine calculations easily and rapidly.

The determination of a and b is not a matter of guess or iteration. In this statistical method, an underlying assumption is that the value of x has negligible error or is free from error. It assumes that the deviation lies principally in the measurement of y, in this case, the emissions.

Other assumptions in the method exist, but the main point here is that the values of a and b are mathematically determined and depend only on the original test data. If the dependence of y on x should change because of a change in operations, system degeneration, or faulty determination of x, the best line will no longer be valid.

4.5.2.2 Multiple Linear Regression

More than one parameter may influence the value of y (the emissions). The equation for y may then appear as:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + ... + b_kx_k$$

for k parameters. This is the more likely case in emissions applications and techniques of multiple linear regression can be used. The approach is similar to that given for simple linear regression, but a set of k simultaneous linear equations are solved to determine the values of b_o to b_k. In multiple regression, the effect of one parameter on the emissions can be determined while the other parameters are kept constant.

Linear regression statistical techniques have been used widely to develop PEM system models. Published examples most often address monitoring NO_x emissions from industrial boilers. Evans (1995) has developed a PEM NO_x model for a gas-fired boiler using two parameters, % excess O_2 and flue gas temperature. Macak (Macak, 1988), using multiple linear regression techniques, developed a model for a natural gas-fired boiler using three equations, each used over different load ranges, and each using two to three different parameters.

4.5.2.3 Higher Order Multiple Linear Regression

Higher order linear models may be used to provide curve fits to data (Draper, 1981). In the case of more than one parameter, the regression expression may include higher orders of the input variables and incorporate expressions such as:

$$y = a + bx + cx^2$$

For multiple input parameters both polynomials and polynomial cross-products may be included:

$$y = b_o + b_1x_1 + b_2x_2^2 + b_3x_1x_2 + b_4x_1x_2^2 + ...$$

These expressions are termed linear regression equations since they are linear in terms of the regression coefficients. The first expression is a second order linear equation. The second expression is a third order linear equation.

4.5.2.4 Nonlinear Least Squares Regression

Nonlinear models express the model output (emissions) as a nonlinear function of the regression coefficients (a, b,...). The nonlinear function may be a power function, or a logarithmic or exponential function of the regression coefficients. Examples of nonlinear models include:

$$y = a + x^b$$

$$y = a + \log(bx)$$

$$y = a + e^{-bx}$$

The constants for nonlinear models are determined by iteration techniques similar to those in linear regression. Some non-linear forms present significant mathematical complexity and require numerical methods rather than analytic solutions.

Many more mathematical options are available in the nonlinear and multiple order curve-fitting techniques. One may be able to represent the initial input data well with such models, but a danger exists in "overfitting" the data. One can "correlate" or fit a curve between any two sets of numbers, but if no actual relationship exists between them, future predictions will not necessarily be valid.

Clapsaddle (Clapsaddle, 1995, 1996) has used polynomial expressions to represent emissions in gas and oil-fired boilers. Four to six parameters such as fuel oil flow rate, air flow rate, excess O_2, fuel gas flow rate, air damper position, air heater outlet temperature, fuel bound nitrogen, were used in the various models. Snyder, et. al. (Snyder 1996) used up to five parameters in nonlinear models for predicting NO_x and CO emissions from stationary gas turbines.

4.5.2.5 Neural Network Models

Neural network models have been applied recently to model source emissions. Although the neural network methods are inherently mathematical, analogies can be made to biological learning processes. The regression methods discussed so far provide a model that is calculated by using a set of equations. In the neural net method, the model constants are not calculated, but are determined by iteration. The constants in the model are varied incrementally until a set of constants is obtained that will reproduce the actual emissions of the input data set. Least squares regression methods are still used in neural net models to minimize the residual differences between the test emission data and the model predicted emissions.

In developing neural network models, extra sets of constants are introduced into what are called "hidden layers (or nodes)." These constants, in conjunction with nonlinear functions, can weight the importance or unimportance of different input parameters in contributing to a given result. This "weighting" also is done by an iterative process.

This weighting process is similar to what neurons do in the brain, hence the word "neural."

Neural network procedures are somewhat of a "brute force" approach in statistical model development. The procedures use the iterative capabilities of the computer to choose optimum constants that best represent how a process operates. The method is powerful since most process operations are complicated and the interrelation between input parameters is not always well understood. The approach is similar to using a computer to numerically integrate an integral that is too complex to solve analytically.

Neural network models do offer some greater flexibility in optimizing system operations. Since the contribution of the various parameters to the operations is better understood, this information can be fed back to improve system performance. Neural network process optimization models have been said to have been developed for the chemical, petrochemical, semiconductor, and mining industries (Keeler, 1993).

In one study, 21 input parameters, selected from 120, were used to develop an NO_x prediction model for a gas fired boiler (Collins, 1994). Clements, et. al. (Clements, 1996) applied both multiple linear regression methods and neural network techniques to develop PEM models to predict NO_x, CO, O_2, and stack gas flow rates for gas turbines and reciprocating gas engines. In this study comparing the two types of models, regression coefficient (R^2) values were found to be better for the neural network analysis than for linear regression analysis. **Note:** R^2 values give a measure of the "fit" of the model to the data, but are not necessarily an indicator of which model will provide the best prediction from new data (Evans, 1995).

4.5.3 Model Development

A typical approach to model development is to first review all potential operational parameters that affect emissions, determine the full operating range for each parameter, examine potential cross parameter interaction, and then develop a test matrix to evaluate the effect of parameter changes on the emissions (Clapsaddle, 1996). The emissions are then characterized according to the test plan and a regression model developed from the test data. Evans (Evans, 1994) proposes a similar approach that emphasizes care in the selection of model parameters. The test must concentrate on parameters that have an effect on emissions. Inclusion of parameters that have negligible effects will complicate the test without commensurate improvements in the model. The main problem in developing models is in not recognizing parameters that can affect emissions. This "lurking parameter", being as simple as an open or closed damper, can easily invalidate any model (Evans, 1994).

A model should be developed over a sufficient period of time where a full range of operating conditions can be correlated to the emissions. During this time both accurate emissions data and sensor data are required. If either inaccurate sensor or emissions data are used to build the model, the model itself will be inaccurate.

Usually more than one model is examined when developing a PEM system. Different combinations of parameters and both linear and nonlinear regression equations may be used to examine those having the best fit with the data. An examination of residuals, confidence intervals, and regression coefficients typically are examined in the evaluation process (Evans, 1995).

A relative accuracy test audit (RATA) used to certify CEM systems is not necessarily sufficient to validate a PEM model (Eghneim, 1996). The RATA normally is conducted at only one operating condition of the source. For a PEM system, if that operating condition were to be one under which the correlation were developed, the system should obviously pass. A truer evaluation would be to conduct a RATA, or RATAs, at operating conditions different from those used to develop the correlation. To be "predictive," the model must provide true emissions values from parameter data not previously provided to the model.

4.5.4 Model Quality Assurance

In NSPS requirements for operations monitoring, sensor calibrations are required to be checked annually. The manufacturer of a sensor is expected to deliver a product to specified levels of precision and accuracy. These levels are chosen to be within an acceptable range for the intended application, usually ±5% of reading. However, users often assumed incorrectly that the performance of a sensor will remain constant with time. The calibration may drift over time, the sensor may become fouled, or it might not work at all. Plant maintenance routines provide for inspection of these devices, but the sensors most critical to plant operation usually receive the most attention.

If a parameter monitoring program is to be initiated, the sensors used to provide parameter values for a

model or correlated relation must provide values at consistent levels of precision and accuracy. To do otherwise leads to faulty data, just as would a poorly calibrated or malfunctioning analyzer of a CEM system. A quality assurance program instituted to assure that the sensor data continues to be valid is as essential in PEM systems as a preventive maintenance program is in a CEM system (Macak, 1996, DeFriez, 1996). The "once yearly" check for a sensor may no longer be sufficient and quarterly or monthly preventive maintenance procedures may be necessary to ensure the continued validity of the model.

PEM systems do, however, have the capability of performing self-diagnostics and making adjustments for poor sensor data. If redundant sensors are installed in a system, the PEM system might switch to another operating sensor after one fails. Algorithms can be instituted to perform cross-checks, or reality checks for sensors. Historical data might even be substituted for missing data until a faulty sensor is replaced or the PEM system may model the sensor data itself from other input variables. However, the regulatory acceptability of these substitution procedures has not been addressed in most state or federal monitoring programs, except for a few instances (for example, see 40 CFR 75 Appendix C).

EPA historically has required daily calibration checks for monitoring instrumentation so as to provide for legally defensible data for each operating day. The necessity of providing a means for assuring data quality on a routine basis is as important in PEM systems as it is in CEM systems (Eghneim, 1996).

4.5.5 Model Limitations

The availability of least squares regression and neural net software enables one to correlate any two data sets by a variety of methods. However, the ease of doing this can create problems if basic assumptions of the method are ignored. Using extensive sets of past performance data may not be valid if the data were obtained under different or unknown operating conditions. If site conditions change (such as a change in emission controls or a change in fuel type) new test data must be obtained.

Including or excluding parameters without examination or justification can result in complicated models that are not robust - they may be valid for only one set of conditions, give the same emissions results for different sets of parameters, or give nonsensical results outside and within the expected range of applicability. The key for a good PEM model is to design a thorough experimental test program that examines the effect of selected parameters on emissions and to understand the statistical correlation methods and assumptions used to mathematically develop the model (see Evans, 1994, 1995).

4.6 Issues in Parameter Monitoring

The use of parameter monitoring techniques to determine source emissions offers an alternative to the installation of CEM systems. Parameter-based models can be relatively inexpensive to develop and they can provide process information and feedback that can be used to increase plant efficiency and reduce emissions.

Decisions regarding the use of parameter methods, particularly the PEM systems, often reduce to the issue of PEM system versus CEM systems. Predictive methods have been promoted actively by commercial firms that market the technique. Introducing an innovative technique is difficult, and marketing programs in this area have exhibited biases with respect to both technical and commercial issues in order to gain industry and agency acceptance (e.g., Samdani, 1994, Steven, 1994). One particular marketing point that is emphasized frequently is the relative cost of CEM systems versus PEM systems, with the implication that PEM systems constitute a lower cost option. As we shall see in Chapter 6, technical applicability is the most important criteria for selecting a monitoring system and initial capital cost should not be the sole criterion.

Parameter models do offer some significant advantages as a monitoring technique, but one must remember that a model is still a model. It can give present information based upon past data or it can predict future information based upon hypothetical data. But a model is always tied to the past operation of the process and the present sensor data. This is in contrast to manual reference test methods or CEM systems, which provide measurements that are relatively independent of the process and its past history.

As we have seen above, predictive systems are developed by correlating parameter data with emissions data over a range of conditions. The correlation will continue to be valid if those conditions are maintained and the sensors provide input data at the same level of quality as provided during the correlation testing. However, of interest to both plant operators and regulatory agencies is what

happens under upset conditions, what are the emissions when the process is not operating properly (see for example, Macak, 1996). Since most correlations are not developed under such conditions, the model predictions will either be incorrect during the period of malfunction or the model may flag the data as "missing." In the first case, the data will be misleading (Figure 4-5b); in the second case, no data will exist (Figure 4-5c).

The scenarios of Figures 4-5a and 4-5b may be convenient for the source required to report periods of excess emissions, but not desirable for the regulatory agency. A more complete model would be able to determine that the upset occurred through appropriate sensing devices, and would then switch to an alternate model or algorithm to account for the upset. The problem here is multifold. First, one would have to be aware of all possible upset conditions. One would then have to either initiate or simulate the possible upset conditions and obtain reference emission data to develop the alternate models. This could be prohibitively expensive, or impossible if one could not or did not wish to produce the upset conditions during the development effort. Another approach might be to establish "control limits," or limiting conditions for the model. When the process operates outside these limits, the model will be out-of-control and data cannot be used. Such limits would be analogous to the 40 CFR 60 Appendix F out-of-control limits for a CEM system.

For example, in gas turbine models, NO_x emission predictions are based upon the inherent assumption that the turbine is maintained and operated under the conditions under which the model was developed. Should water injection nozzles become plugged, or water distribution in the turbine become uneven, the model becomes invalid. The wear and tear on a system, the normal degeneration of system components due to continual operation will remove the system from the baseline conditions from which the model was developed. These issues are similar to those associated with CEM systems, since a CEM system must be maintained properly to operate under the conditions at which it was certified. As with CEM systems, a program of quality control, of checking model performance and sensor performance, must be instituted to ensure that the model continues to represent current conditions.

PEM model maintenance issues are therefore very important. Just as with CEM systems, when a component is modified or replaced, the question of recertification arises when the model is modified. Agency guidance in this area is still developing, but questions posed by Clappsaddle are pertinent (Clapsaddle, 1995): "Can periodic adjustments be made to the PEM model equation (without recertification)? If a RATA on the PEM shows inaccuracies, can the PEM model be adjusted and then accepted until the next required quality assurance (QA) audit? How many times can a PEM fail a QA audit before a regulatory agency requires that the PEM be replaced?" Other questions arise with regard to techniques used in "sensor validation." If a sensor is replaced, is the model still valid? Is recertification required? If a sensor fails and sensor data are reconstructed to substitute and maintain data availability, should the model be certified under those conditions and other possible sensor data substitution scenarios? (See DeFriez, 1996 for a discussion of sensor issues.) If a model contains different algorithms for different operating conditions, should the model be certified at each operating condition?

The cost issue has become distorted considerably in PEM system vs CEM system arguments. PEM system costs are often compared inappropriately to the costs associated with CEM systems installed to meet the requirements of the Part 75 acid rain program. In Part 75, the hardware precision and accuracy requirements and detailed data acquisition and handling systems (DAHS) specifications necessary to legitimize data for allowance trading justified higher costs. Systems installed to meet the NO_x or VOC monitoring requirements of a state Title V permit program are not required to meet such stringent specifications, and their costs are consequently much less.

Many CEM system suppliers now offer CEM systems at prices comparable to commercial PEM systems. When one considers the correlation testing necessary to develop a PEM system model and the certification testing necessary to validate the model, initial capital costs are often comparable. Also, if the original correlation becomes invalid due to process changes or system degeneration, the correlation testing would have to be redone. The ongoing quality assurance costs can be comparable between the two methods. These cost issues are further discussed in Chapter 6 of this manual.

Those required to monitor non-criteria pollutants may have the flexibility to choose between a CEM and PEM system to meet the requirements of future rulemaking. Depending on the application, the two techniques can be competitive both in terms of cost and accuracy. However, one of the most powerful

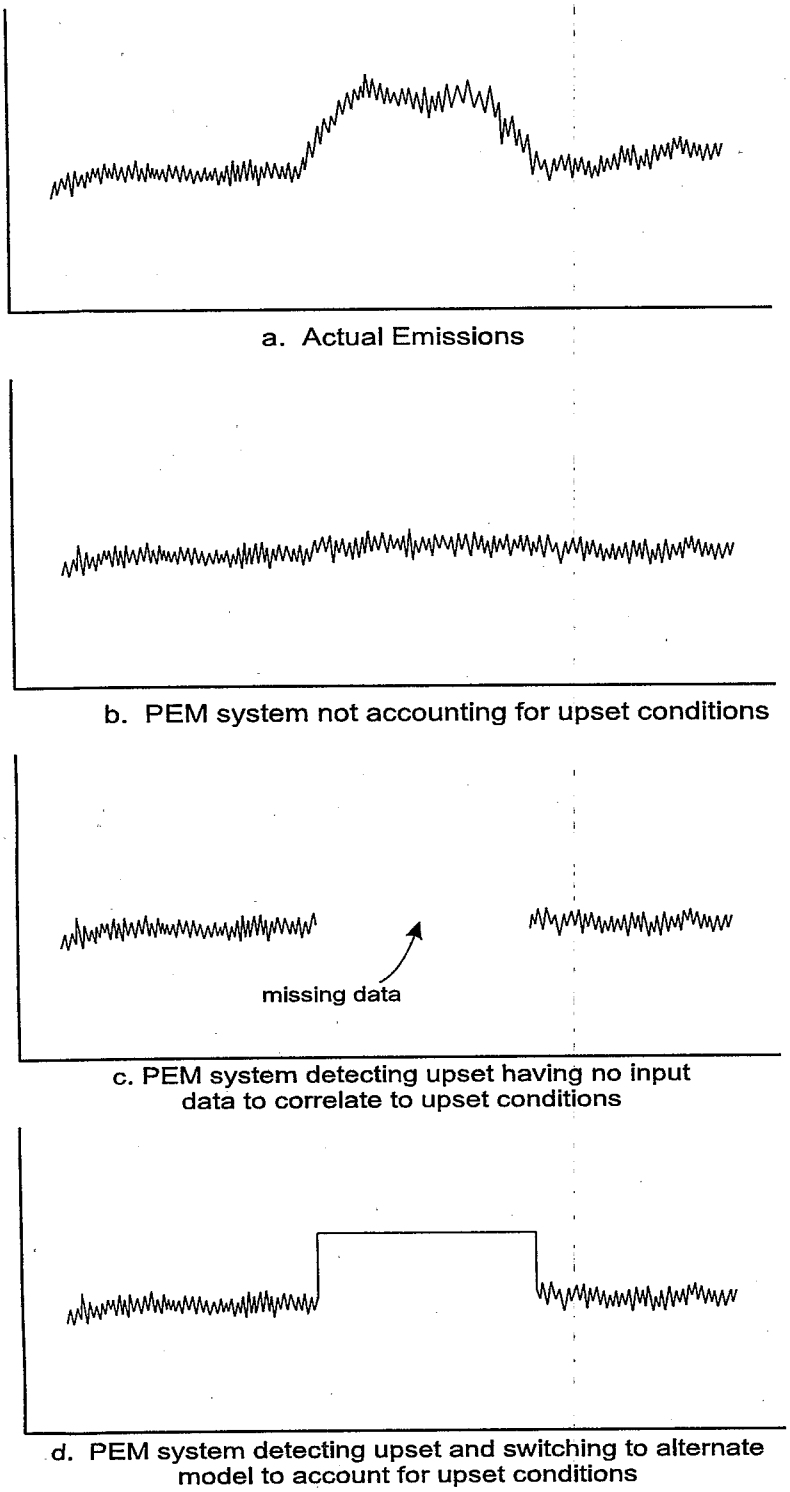

Figure 4-5. Emissions calculations (PEM system predictions) based upon upset conditions not accounted for by the model.

options is the combination of two methods (DeFriez, 1996, Macak, 1996). With a combined CEM/PEM system, the PEM system can serve as a backup to the CEM system, as in the prescribed techniques can be competitive both in terms of cost and accuracy. However, one of the most powerful options is the combination of the two methods C-EM/PEM system, the PEM system can serve as a backup to the CEM system, as in the prescribed methods of the acid rain CEM program (40 CFR 75). Or, a CEM system can serve as a backup to a PEM system. When a sensor validation program causes the PEM system to invalidate data and report missing data due to failed sensors or an unrecognized operating condition, the CEM system can fill in the missing data gap. The CEM system can provide the data where it may be most needed, the period of plant upset conditions not accounted for by the PEM model.

The final decision in choosing a monitoring method, whether a CEM or a PEM system, depends upon how the data will be used and the constraints of the application. Questions need to be asked about whether a DCPL or predictive model will meet monitoring requirements, will the method be sufficient for demonstrating compliance, or will the data be accurate enough for a trading program? A consideration of these questions should involve an evaluation of cost, regulatory, and technical issues; none should be considered solely.

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Chapter 5
System Control and Data Recording - Data Acquisition and Handling Systems

A data acquisition and handling system (DAHS) is a combination of hardware and software that is used to record data and generate reports for submission to the regulatory agency. A properly designed DAHS also can provide warnings of CEM system fault conditions and excess emissions so that adjustments and repairs can be made in a timely manner. The DAHS is considered an integral part of the CEM system and must be included as part of the CEM certification and audit procedures. Because CEM data are a key enforcement tool used by EPA and local agencies, emissions reports must be prepared in a manner that accurately reflects the quality of the data and any anomalies that occurred during the reporting period (McCoy, 1986).

Although not generally considered part of the DAHS, control of CEM system functions such as calibration, probe blowback, and probe switching (for time sharing systems) is often performed by the same hardware and software that performs some data acquisition functions. For example, the same programmable logic controller (PLC) may be used to calculate emission rates and to control calibration cycles. Decisions about the CEM control hardware and software must be made with a consideration of how it will affect the ability of the user to change DAHS vendors in the future (see Commercial PLCs section). This chapter contains discussions of CEM system control and data acquisition functions.

The complexity of the DAHS required for a given application depends on the number of emission parameters being monitored and the applicable reporting requirements. Three basic options for handling emissions data are described in this chapter: a simple data recording device (stripchart or datalogger), a plant mainframe computer (often used to implement a distributed control system (DCS)), and a commercially available DAHS. The design elements of commercial DAHSs are described in detail.

5.1 Option 1: Simple Data Recording Device

In the case of very limited data reporting requirements, a simple stripchart recorder or data logger may be adequate. Digital stripchart systems will average data, calculate emission rates, and display the data either graphically or in tabular form (Figure 5-1). Often they have some data storage capability so that data can be downloaded periodically to a personal computer. The simple recording device may be the preferred option if the facility is required to monitor and certify compliance, but is not required to submit summaries of emission data or CEM system quality assurance data to the regulatory agency. A PLC or other device may be necessary to control calibrations and sampling, but in some cases these functions can be controlled by the gas analyzer itself.

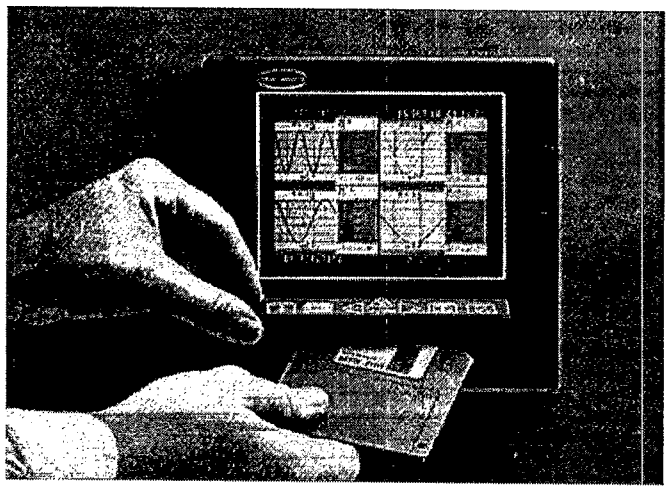


Figure 5-1. Odessa paperless stripchart.

To quantify negative zero drift during calibrations, the recorder scale must be capable of providing concentration results well below zero. For example, 40 CFR, Part 60, Appendix F CEM quality assurance procedures require that a CEM system be declared "out of control" if the calibration drift exceeds four times the drift limit in the applicable performance specification.

For example, if a CEM system with a range of 0-1000 ppm was subject to a drift limit of 2.5% of span during the Performance Specification Test, the DAHS would have to be capable of displaying a reading at least as low as -100 ppm (-0.025 x 4 x 1000 = -100).

Some regulatory agencies no longer accept stripchart data for reporting purposes (even as a backup system) or they place restrictions on the resolution of the recorder. Therefore, consultation with the regulatory agency must occur before deciding to use this option.

Choosing a simple data recorder will reduce the initial capital investment in the CEM system, but it may be more costly in the long run. If the CEM system does not have a method of recording fault conditions or process operating status, interpreting the emissions data retroactively for CEM system or process upset conditions may be difficult and time-consuming. Thus, the validity of the data for extended periods of time could be questionable. Without a DAHS, the user will be required to keep up with the calibration and other quality assurance data manually, making implementation of a CEM system quality assurance plan more difficult. Also, a backup recorder should be used to prevent failures in the data recording device from causing violations of CEM system downtime provisions.

5.2 Option 2: Plant Mainframe Computer System

A limited number of facilities have opted to develop their own DAHS using the plant mainframe computer system. Plant process control systems typically are equipped with excess data recording and storage capability. The plant internal programming option is attractive because the CEM data can be integrated easily with the other plant data display and backup systems. The programming also can be tailored to meet the specific needs of the plant operators. The downside to this approach is that the extra programming required to keep up with CEM emission rate calculations, alarm conditions, calibration data, emission data validation, and report generation can be underestimated. An internally programmed system may not be as flexible as a commercial product and may need periodic reprogramming to keep up with changing regulations or operator needs. When choosing between internal programming and a commercial DAHS, the user should examine carefully all of the functions offered by commercial systems and make an honest appraisal of the cost and delivery schedule issues associated with developing the programming in-house. Commercial DAHS provided either by the CEM vendor or by an independent DAHS provider have been found to be more cost effective by most CEM system users.

5.3 Option 3: Commercial DAHS

A DAHS is a stand-alone system that is used to display data in units of the emission standard, provide alarms, and prepare reports for submission to regulatory agencies. It can be used by the operator to produce edited emission summaries, excess emission reports, alarm reports, and CEM system downtime and corrective action reports. A typical system (Figure 5-2) consists of a personal computer, a data interface (typically a PLC or datalogger), a backup data storage device, and a printer. The DAHS computer may be connected to a local area network (LAN) and/or it may be equipped with a modem for remote access.

Since the implementation of the new source performance standards (40 CFR, Part 60) and the Acid Rain Program (40 CFR, Part 75), CEM system and DAHS vendors have made great strides in the reliability, flexibility, and utility of personal computer-based DAHSs. Recent additions to DAHS software packages include reporting requirements for 56 CFR 7134 (BIF Rule), 40 CFR 63 (MACT standards), 40 CFR 503 (sewage sludge incinerators), and the revised standards for hazardous waste incinerators. Early DAHS software was written specifically for each installation, but most vendors now have standard software products that can be configured by the user for each regulatory application.

If the user has special data reporting requirements from an unusual permit condition or a state rule, the software provider may need to perform custom programming. Such custom programming can be costly for the user and can lead to software "bugs." If possible, the user may propose a more standardized reporting format to the regulatory agency to avoid custom programming.

DAHS functions and some typical hardware components are described in the following sections.

5.3.1 Emission Data Recording

Some gas analyzers and sensors send digital signals directly to the DAHS and others send analog signals (usually 4-20 mA) that must be converted to a digital value and scaled to the appropriate units (concentration, flow rate, temperature, etc.). Concentration and flow rate data are used to calculate emission rates in units of the emission standard. The units of the emission standard vary according to the type of facility, the applicable regulation, or the permit

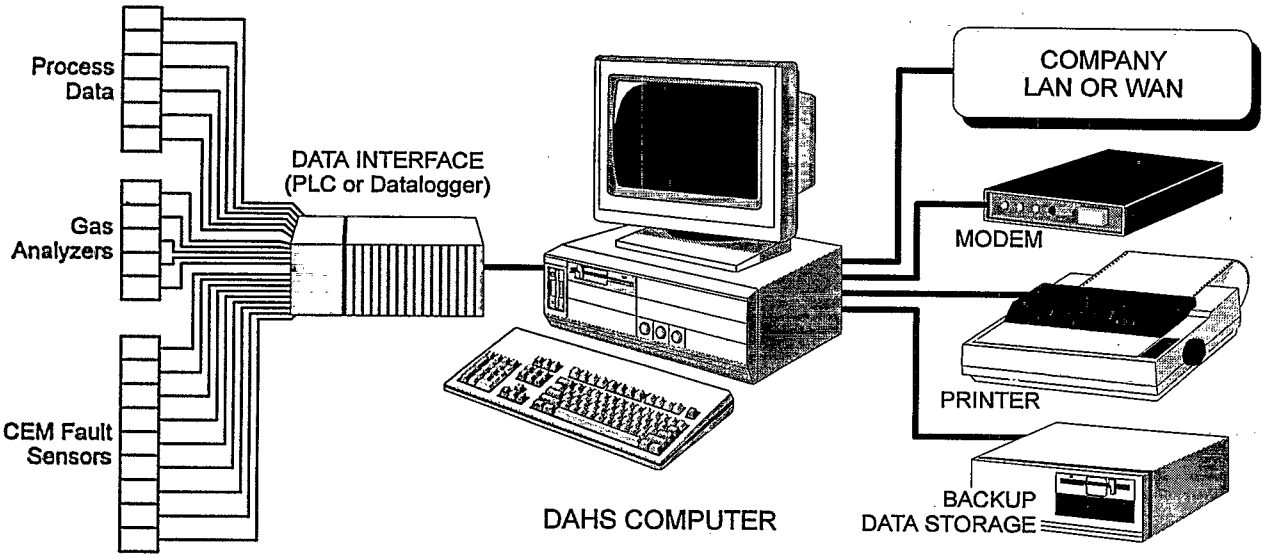


Figure 5-2. Typical DAHS system.

conditions. Some common units for emission standards are:

- ppm_v of pollutant
- ppm_v of pollutant corrected to a standard O_2 dilution basis (e.g., ppm_v at 7% O_2)
- ppm_v of pollutant corrected to a standard CO_2 dilution basis (e.g., ppm_v at 12% CO_2)
- lb of pollutant/MMBtu of fuel combusted
- lb of pollutant/hour
- lb of pollutant/lb of product

A more comprehensive discussion of the units of the standard are found in Appendix E.

Because analyzer measurement ranges and the parameters used to calculate emission rates can change over time, most DAHSs include a menu system to allow the user to scale the analyzer channels and edit the emission rate calculations. Emission rate calculation errors are not uncommon, therefore the emission rates should be verified with hand calculations when the DAHS is first installed and after each change of the calculation parameters.

The applicable monitoring regulation or permit conditions should state the minimum frequency of data collection and recording for each parameter; if not, it should be discussed with the regulatory agency before the DAHS is chosen. Minimum data collection frequencies can be from once per 10 seconds to once per 15 minutes, depending on the variability of the emission parameter and the response time of the CEM system. If the sampling frequency is high, use of a PLC or data logger may be necessary to preserve processor time on the DAHS PC. The minimum frequency of data collection may be different from the minimum frequency of data recording. For example, BIF regulations for monitoring of total hydrocarbons require that data be collected at least once each 15 seconds, but average data values need to be recorded as one-minute averages. For sources subject to 40 CFR, Part 60 monitoring requirements, the minimum data collection frequencies can be found in section 60.13.

The averaging periods should be flexible to allow easy data collection during quality assurance testing. Having the ability to print real-time one-minute averages simplifies conducting and documentation of cylinder gas audits and relative accuracy tests.

5.3.2 Emission Data Display

The main viewing screen of the DAHS should have a real-time data display that is easy for operators to read. The screen should show emissions data, CEM system status (on-line, off-line, calibrating, etc.) and the status of alarms. If the DAHS computer is not located near the CEM system hardware, a second display terminal should be located near the gas analyzers for quality assurance checks and trouble-shooting. Often the reading on the front panel of an analyzer does not match the reading on the DAHS screen due to small signal conversion errors or automated calibration corrections. Therefore, the analyzers should be tuned to provide accurate results using results from the DAHS. A PLC or data

logger located near the analyzers often can be used as a display device for troubleshooting.

Most DAHS vendors include software that allows the user to look at historical trends in the data (Figure 5-3) for user-selectable intervals and averaging periods. Trending of different combinations of emission and operating parameters can be used to determine whether changes in emissions data are linked to plant operation or to CEM system operation. Key plant operating parameters such as production rate, temperatures, or control device parameters can be trended with emissions data for troubleshooting. The trending software also may be helpful in determining the nature of emission exceedances when preparing emission reports for the regulatory agency. If the plant computer control system has ample capacity, some users may prefer to send CEM system data from the DAHS to the plant computer so that plant operators can use display and trending software that is familiar to them and already available at their workstations.

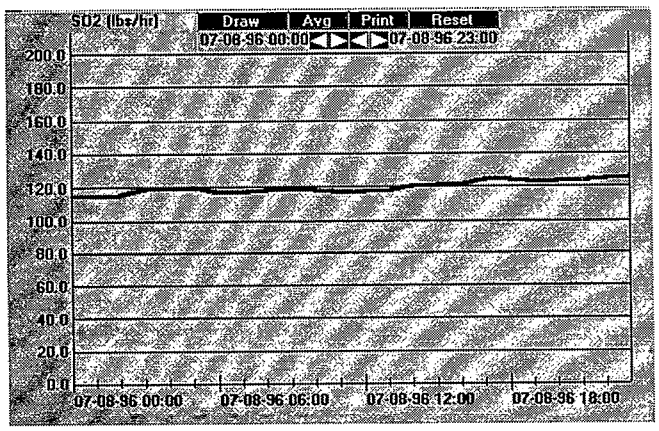


Figure 5-3. Example historical trend screen.

5.3.3 Sampling System Control

The DAHS software and/or computer may be used to control routine sampling system control functions or it may simply monitor control functions that are conducted by a PLC. If the CEM system uses an extractive sampling system, periodic purging of the sample probe with compressed air to remove particulate matter from the probe tip filter may be necessary. The duration and frequency of air purges depend on the particular type of emission source and on the source operation. After the CEM system installation, it may require several months of operation to determine the optimum purge duration and frequency settings. These settings should be configurable by the user on the DAHS computer, PLC, or datalogger. Likewise, CEM systems that perform time-sharing of sample probes (i.e., using the same analyzers for more than one emission point) should include a method for adjusting the frequency of probe switching. For both time-sharing and air purges, the emissions data will be invalidated for short periods. Some DAHS systems use "sample and hold" circuits to keep the analyzer response constant during purges, while other DAHSs label the data as "invalid" and do not include it in averages. Also, the time required for the sampling system to be completely purged can change over time due to filter plugging or changing sample pump performance. The CEM system user periodically should verify that the purge times used by the DAHS are adequate to ensure that only representative sample data are being recorded.

5.3.4 Calibration Control and Recording

Automatic daily zero and span calibrations of the CEM system may be controlled by the DAHS or the DAHS may monitor the activity of a PLC. For calibration using cylinder gases, the DAHS should have a feature that easily allows the user to edit the initiation time, concentration values, and the duration of each calibration gas injection. For each calibration standard, the following information should be recorded:

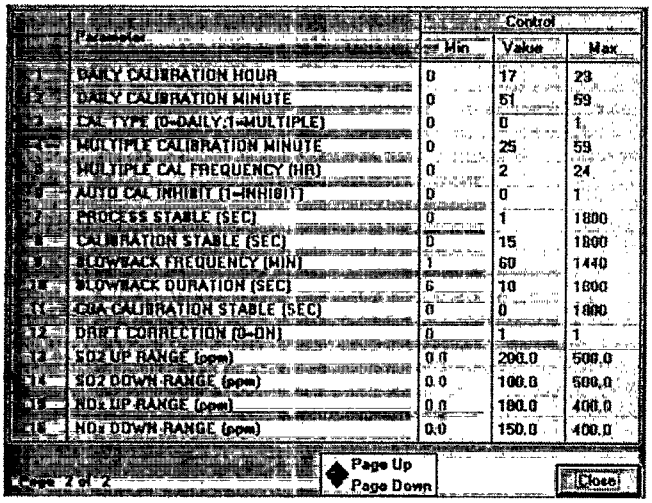
- time and date
- value of the calibration standard
- instrument response to the calibration standard
- amount of calibration error (as a percent of instrument span)

An example calibration cycle configuration screen is shown in Figure 5-4.

The DAHS also should allow the user to initiate an automatic calibration cycle at any time. This feature is especially useful when CEM system data are in doubt or after any recalibration or repair.

Rather than adjusting the zero and span of an analyzer at the instrument itself, some users prefer to make zero and span adjustments by automatically applying correction factors using the DAHS after each calibration check. When such adjustments are made, the calibration report must include the values used for the calibration adjustment. Automatic calibration adjustments apply only to data collected <u>after</u> a given calibration and before the next calibration adjustment. Retroactive calibration adjustments generally are not allowed. The accumulated amount of calibration adjustment made by the software should be limited so that degradation in CEM system performance can be detected. An excessive soft-

ware correction is a sign that the CEM system hardware should be inspected. Typically, a DAHS will generate an alarm when the zero or span software correction exceeds 5 or 10 percent of span.



	Parameter	Control		
		Min	Value	Max
	DAILY CALIBRATION HOUR	0	17	23
	DAILY CALIBRATION MINUTE	0	51	59
	CAL TYPE (0-DAILY,1-MULTIPLE)	0	0	1
	MULTIPLE CALIBRATION MINUTE	0	25	59
	MULTIPLE CAL FREQUENCY (HR)	0	2	24
	AUTO CAL INHIBIT (1-INHIBIT)	0	0	1
	PROCESS STABLE (SEC)	0	1	1800
	CALIBRATION STABLE (SEC)	0	15	1800
	BLOWBACK FREQUENCY (MIN)	1	60	1440
	BLOWBACK DURATION (SEC)	6	10	1800
	CGA CALIBRATION STABLE (SEC)	0	0	1800
	DRIFT CORRECTION (0-ON)	0	1	1
	SO2 UP RANGE (ppm)	0.0	200.0	500.0
	SO2 DOWN RANGE (ppm)	0.0	100.0	500.0
	NOx UP RANGE (ppm)	0.0	180.0	400.0
	NOx DOWN RANGE (ppm)	0.0	150.0	400.0

Page 2 of 2 Page Up Page Down [Close]

Figure 5-4. Example calibration cycle configuration screen.

5.3.5 Alarms

All commercial DAHSs can be configured to provide alarms for excess emissions and CEM system fault conditions. Depending on the design of the DAHS, the alarms may be triggered at the DAHS computer, PLC, datalogger, or at the analyzer itself. The DAHS is equipped with alarm acknowledgments that allow the user to enter the reasons and corrective actions for alarm conditions. The alarms, reasons, and corrective actions can be reviewed periodically to identify recurring problems with the process or CEM system operation. Triggers for excess emission alarms can be set at lower setpoints or at shorter averaging periods than the emission standard so that corrective action can be taken before an actual emission exceedance occurs. Some excess emission indications during conditions such as unit startup/shutdown or equipment malfunctions may be exempted by the applicable regulations. CEM system operators have found that when data are examined only during the preparation of quarterly emission reports, incomplete records often lead to the inability to determine the reason and corrective action for each exceedance. For this reason, commercial DAHSs contain lists of numbered reason codes that are entered by the operator as part of the alarm acknowledgment procedure. The operator also may opt to enter a reason code for "unknown" or manually enter a reason that is not on the list. The list of reason codes for a given facility should be reviewed periodically to make sure that the list is complete and that the reasons are adequately descriptive. Some regulatory agencies can offer guidance on which reasons constitute "excused" exceedances. Some example excess emission reasons are provided below:

- bag leak
- baghouse blowback
- air damper malfunction
- plugged spray nozzles
- start-up
- shut down

The use of CEM system fault alarms can reduce the time required for diagnosis and repair as well as reducing the CEM system downtime. Fault alarms also can be used to invalidate questionable emissions data automatically, simplifying report production. Some common CEM system fault conditions are listed below:

- analyzer flame-out
- sample flow low
- sample vacuum high
- calibration gas pressure low
- sample line temperature low
- condenser temperature high
- water in sample line - pump shut off
- dilution air pressure low

5.3.6 Plant Computer Interface

As discussed in Option 2: Plant Mainframe Computer System, the plant computer control system can be used to display CEM data in a manner that is useful to the process operators. Likewise, plant operational data should become part of the DAHS. The most useful application of plant data is for determining when the process is on-line, off-line, or in a startup or shutdown condition. Threshold levels for such parameters as steam flow, fan speed, or stack temperature can be used by the DAHS to automatically mark the data as valid or invalid for emission reporting purposes. In addition, EPA guidelines for open market trading programs require correlation of emissions data with the activity level (percent capacity) of the emission source. Having production unit and control device operational data in the database while preparing periodic emission reports also can be useful in explaining anomalies in the emissions data or "unknown" reason codes for excess emissions.

5.3.7 Report Generation

Commercial DAHSs are designed primarily for sources subject to monitoring provisions of 40 CFR Parts 60 and 75. These monitoring requirements include detailed reporting requirements for emissions summaries, excess emissions, CEM system downtime, and CEM system data quality assurance test data. Even if the applicable reporting requirements do not specify detailed reporting, the reporting software that already has been developed for other applications can be very useful for internal quality assurance programs. DAHS systems include editing functions that allow the user to review questionable data and mark it as "valid" or "invalid" based on what was known about the CEM system and plant operation at the time the data were collected. In all cases, the raw unedited data files are retained separately for later reference.

5.3.7.1 Data Flags

During data collection, the DAHS labels each discrete emission data average according to the quality of the data or the status of the CEM system at the time that the data were collected. When emission reports are prepared, the flags allow the editor to sort data by its designation. DAHS vendors use different systems for labeling, but a typical list of data flag designations might be:

- valid data
- invalid data due to an alarm condition
- questionable data due to alarm condition
- process unit off-line
- process unit in startup or shutdown condition
- calibration in progress
- analyzer logged off-line for maintenance or other QA activity
- substituted backup reference method data during extended CEM system downtime

The data flags allow the DAHS software to calculate percent data availability, process unit on-line hours, and emission averages. The data can be sorted to compile summaries of excess emissions, CEM system downtime, and process status summaries.

5.3.7.2 Emission Summary Reports

To prepare a summary of emissions data the user must first review all of the data for the reporting period and resolve all issues of questionable data quality. Preparation of this summary may involve reviewing the plant or CEM system operation and maintenance logs. When all data have been sorted correctly, the DAHS automatically recalculates averages and produces data summaries based on the data that have been through the review process. The editing function is particularly useful when calculating long-term or rolling averages such as 24-hour block averages or 30-day rolling averages from one-hour average values.

5.3.7.3 Excess Emission Reports

Most monitoring regulations require the CEM system operator to report the time, date, magnitude, reason, and corrective action for each exceedance of the emission standard. A common feature of almost all DAHSs is the ability to produce automatically reports summarizing excess emissions for a given reporting period. The reason and corrective action codes entered by the operator are provided for each exceedance. During the review process, the user can edit the reasons and corrective actions based on new information. EPA has produced a guidance document which describes how enforcement agencies use excess emission reports (Paley, 1984).

5.3.7.4 CEM System and Unit Downtime Reports

For each reporting period, the CEM system operator generally is required to report the total hours of unit operation and the percent availability of CEM system data. By monitoring process parameters, the DAHS can easily keep track of when the source is on-line or off-line and in most cases can be used to produce a summary report showing the time, date, and duration of each outage. Using CEM system alarms, analyzer on-line/off-line indicators, and information entered during the emission summary editing process, the DAHS can calculate the percent data availability for each emission parameter and also can produce a report indicating the time, date, duration, reason, and corrective action for each CEM system downtime incident.

5.3.7.5 Alarm Reports

The DAHS can be used to produce a list of all alarms that occurred during a given period, including CEM system faults and excess emissions. This summary list can be used during the emission data review process to ensure that all periods of questionable data are resolved. It also can be used to identify the most common CEM system fault conditions that may require an equipment or procedure modification.

5.3.7.6 Calibration Drift Reports

The DAHS can be used to generate a summary of all zero and span calibration data for the reporting period. This report documents the time of each daily calibration and whether the results are within the applicable performance specifications. Even if the drift results are within specifications, the sum-

mary may indicate a long-term degradation in instrument performance.

5.3.7.7 Data Assessment Reports

For those sources which are subject to the ongoing CEM quality assurance procedures in 40 CFR, Part 60, Appendix F, a requirement exists to prepare a data assessment report (DAR) for each calendar quarter. The DAR contains a summary of all quality assurance activities, including daily calibrations, cylinder gas audits, and relative accuracy tests. The DAR may be reviewed by the enforcement agency to evaluate the status of a CEM system (Von Lehmden, 1989).

5.3.8 Multitasking

The DAHS often is required to perform several functions simultaneously. Some of the competing demands placed on the software are illustrated in Figure 5-5. The DAHS must have a resilient multitasking capability to resolve the competing demands without generating errors or "locking up" (Baranowski, 1995). A procedure called "kernelling" is used by the operating system to prioritize tasks and prevent conflicts. In recent years, many DAHS vendors have moved their software to operating systems such as UNIX or OS/2 which are designed specifically for multitasking and multi-user applications. Other systems that use MS DOS or Windows operating systems rely on PLCs or dataloggers to handle most of the routine tasks such as calibrations, data averaging, and emission rate calculations. Multitasking conflicts often are inconsistent and difficult to trace. Only by interviewing other DAHS software users or by conducting extensive acceptance testing can the purchaser be assured that a vendor's software is free from such conflicts.

5.3.9 Expansion

Early providers programmed DAHSs specifically for each application and any changes in the number of inputs being monitored often required an expensive software modification. Most DAHS vendors now provide software that will allow the user to add gas analyzers, emission rate calculations, alarms, and even additional production units using a series of menus within the software. Each vendor offers a different level of flexibility. Before purchasing a DAHS the user must determine the degree to which the system can be expanded without reprogramming by the vendor. Purchasing extra hardware capacity to accommodate additional analog and digital signals is prudent. After operating the CEM system through the break-in period, many users find adding more input signals from the plant distributed control system (DCS) or providing more fault alarms for the CEM system is helpful in the data review process.

5.3.10 Hardware

5.3.10.1 DAHS Computer

Most DAHS vendors use a stand-alone IBM-compatible personal computer for data storage, display, and the generation of reports. However, vendors who use the UNIX operating system occasionally will install the DAHS software on the plant mainframe computer system. Most DAHS vendors will provide the computer with the DAHS but may allow the user to select or purchase their own computer if the company has a preferred manufacturer. The DAHS computer most often is located in the plant control room so that plant operators can have easy access to the data. This also provides a clean environment, a well-regulated power source, and backup for emergency power.

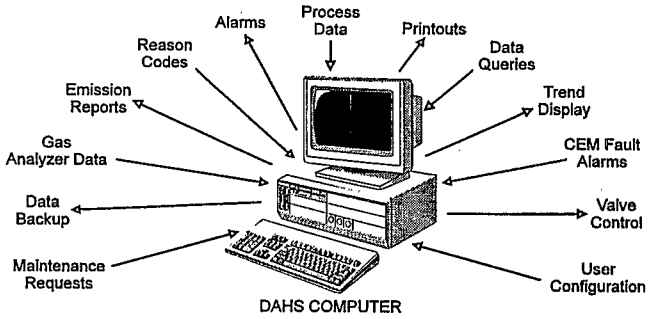


Figure 5-5. Competing demands for processor time.

5.3.10.2 Signal I/O Boards

The least expensive hardware option for processing signals from analyzers and alarms is to use multifunction boards that fit directly into the expansion slots of the DAHS PC or into a chassis that is attached to the PC. Multifunction boards accept multiple analog input signals (from analyzers or other sensors) as well as digital input and output signals (e.g., alarms). Processing the signals places a heavy burden on the PC processor to perform such real-time functions as analog-to-digital conversion, signal scaling, emission rate calculations, and averaging. In addition, the PC may be required to control such functions as calibration and blowback. With the increased burden on the processor, multitasking becomes more difficult. Vendors using multifunction boards may require the user to conduct data review and report generation on a separate computer. Another drawback to this system is that if the PC stops running for any reason, emission data are not collected or stored.

5.3.10.3 Commercial PLCs

Many DAHS vendors use standard PLCs to gather analyzer and alarm signals, calculate data averages and emission rates, and control calibrations and blowback. CEM data are downloaded periodically to the DAHS computer where the data are displayed and stored for report generation. In some cases the PLCs are equipped with memory modules so that data can be stored for days at a time in case of a failure in the DAHS computer. When the computer is restored, the stored data are down-loaded and no data loss occurs. Often plant instrument technicians are already familiar with programming PLCs and may even have backup hardware available in case of a failure. The DAHS vendor should be familiar with the PLC that is chosen for a given application. Often DAHS vendors offer a choice of PLCs, based on the preference of the plant operators. Some common PLC manufacturers that are supported are:

- General Electric
- Allen Bradley
- Siemens
- Modicon
- controllers using the Modbus communications protocol

Since PLCs use different communication protocols, the DAHS vendor should be asked if they have installed other systems using the PLC that is chosen.

A significant advantage to using a commercial PLC is that it may be compatible with DAHS computers from several different vendors. This flexibility makes a change of software vendors possible without purchasing additional hardware. Previous experience by DAHS users in the acid rain program has shown that keeping all options open can be valuable in case the chosen software does not perform adequately (Huberland, 1995).

5.3.10.4 Custom CEM System Dataloggers

Instead of PLCs, some DAHS vendors provide their own custom data loggers that are designed specifically for DAHS systems (Figure 5-6). Some of these systems were developed originally for use at ambient air monitoring stations. The dataloggers perform all of the same functions of a PLC, but often have added features such as real-time data display, enhanced data storage, and battery backup. In the event of a DAHS PC failure, the datalogger will continue to collect data until the PC comes back on-line. The datalogger can be programmed from the front panel or from the DAHS PC using menu-driven software. Because of the added functionality, DAHS vendors can operate several dataloggers (and CEM systems) using one DAHS computer.

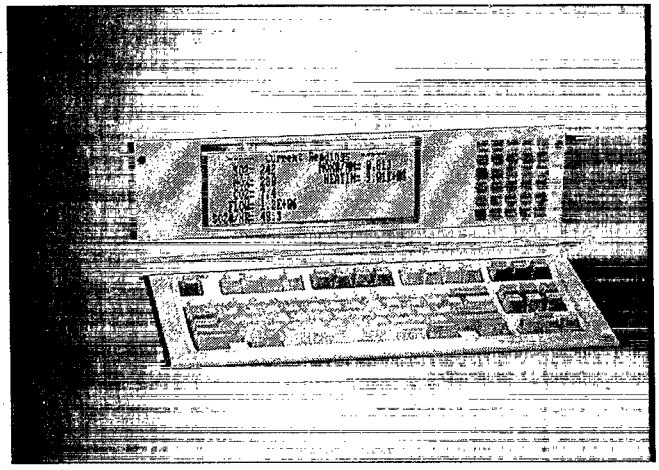


Figure 5-6. Custom CEM system datalogger.

5.3.10.5 Backup Data Storage

The DAHS computer should be equipped with a backup data storage device to prevent data loss in the event of a hard disk failure. Many hardware options are available including magnetic tape, removable hard disks, and optical disks. The backup routine should be automatic and should include a procedure for verifying the integrity of the backup copy.

5.3.10.6 Component Failure Analysis

DAHS failure is among the most common causes of CEM system downtime. Often when a component fails, excessive time is spent finding a replacement and then making the software function properly again. As part of the development of the CEM system quality assurance program, a set of procedures should be established in the event of a DAHS component failure. Determine how long obtaining replacement hardware (I/O card, PLC, datalogger, or computer) takes. If the lead time necessary for shipping could lead to a violation of CEM system downtime limits spare components should be kept on-hand. If a failure of a programmable component (e.g., the PLC, datalogger, or computer) occurs, the software and programming instructions should be kept up-to-date and in a secure location. The operators should practice reprogramming the components to make sure that the procedure is adequate.

5.3.10.7 Remote Access Within the Plant or Company

Many DAHSs now are integrated into the plant local area network (LAN) or company's wide area network

(WAN). For example, the plant environmental coordinator may find monitoring the CEM system and preparing emission reports easier from his or her office. Networking of the DAHS should be discussed with the DAHS vendor at the time of purchase so that communication issues can be resolved. Some functions, such as initiating calibrations, editing data summaries, and entering reason codes, should be restricted with password protection. Often the DAHS provider will install a modem so that diagnostics and software upgrades can be accomplished remotely.

A company may find integration of CEM data from all remote locations into a central location for review and planning purposes advantageous. To integrate results from several locations, the emissions data must be stored in a format that can be converted easily or directly downloaded into a central database (Long, 1995).

5.3.10.8 Remote Access by the Regulatory Agency
Increasingly, state and local agencies are requiring the installation of remote terminal units (RTUs) that allow the agency to monitor CEM system status, source status, and emission data remotely on a real-time basis or to download emissions data via modem periodically (Friedlander, 1992). Remote access usually is accomplished using a separate datalogger that receives concentration and emission rate data from the CEM system. Remote reporting allows the agency to have access to raw data for auditing and monitoring, but the source still is required to submit emissions data according to the regular reporting requirements. Remote terminal units are being used on a limited number of sources by regulatory agencies in Pennsylvania and New Jersey as well as several local districts in California.

5.4 Summary

The ideal DAHS for a given application depends on the complexity of the applicable reporting requirements. A simple stripchart recorder or datalogger may be sufficient for cases where the source is not required to submit detailed emission monitoring reports to regulatory agencies and the monitoring requirements are simple and straightforward. A computer-based DAHS can be an indispensable tool when emission reporting requirements include calculations of CEM data availability, complex data averaging, and generation of reports for CEM downtime and excess emission reasons/corrective actions. A computer-based DAHS can be programmed using the plant mainframe computer or it can be purchased from the CEM vendor or a DAHS vendor.

The best DAHS is one that allows the user to be sure of the status of the emission source, control equipment, and CEM system for the entire reporting period. The first part of preparing emission reports is to answer basic questions such as:

- During what periods was the emission source operating or in a startup/shutdown condition?
- During what periods was the CEM system off-line due to equipment failure or quality assurance and maintenance activities?
- Do any of the reported emission averages need to be recalculated based on new CEM or plant operational data?
- What was the reason and corrective action for each period of CEM downtime or excess emissions?

If the DAHS incorporates sufficient plant operational data and CEM status indicators, these questions can be answered more easily and many labor hours can be saved. Also, the DAHS should include an editor that allows the user to input new information and recalculate emission averages while maintaining the original unedited data in a separate location.

The selection of a particular DAHS can affect the flexibility that the user will have in the future. Some software changes may require reprogramming by the vendor, but many vendors provide software that allows the user to add analyzers, averaging periods, alarms, and even additional emission sources without reprogramming by the vendor. The user also should be cautious about integrating CEM control functions (calibration valve switching, probe blowback, etc.) with the software on the DAHS computer. Combining the control and data acquisition functions in the same software may make the ability to switch DAHS vendors at a later time more difficult and costly. Often CEM system control functions can be performed by a PLC or by the analyzers themselves while the DAHS computer monitors the status of the sampling system and records data.

Finally, determining whether a given DAHS software package will work properly can often be difficult at the time of purchase. Many DAHS users have been forced to switch DAHS vendors shortly after purchase due to poor software performance. The purchaser should interview previous users of the candidate software packages to evaluate the long-term reliability and utility of the software.

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Chapter 6
CEM System Procurement, Installation, and Start-up

Purchasing a CEM system should be a step-wise, methodical process. As we have discussed in this handbook, many .options must be considered and many decisions must be made before a system actually comes on-line. The manager of the CEM project must assimilate and understand the information available on these options, review that information objectively, and choose the options that best meet the project objectives. Many pitfalls exist: one can rely too heavily on the experience of others, become deluded by aggressive advertising, be led astray by low cost factors, or enter the process with decisions already made. As stated earlier, the goal is to choose the best system for the intended application. Achieving this goal reflects on both the technical and the management skills of the project manager.

Several central factors should be considered in the program developed to accomplish this goal (White, 1995a). They are:

1) The design should meet regulatory requirements and be consistent with plant operating requirements.

2) The materials, components, and techniques should be both reliable and durable under the constraints of ambient and effluent gas conditions, and operating conditions.

3) The system should be easy to use, serviceable, and cost-effective in its long term operation.

4) The risks associated with existing and new technologies applied to monitoring non-criteria pollutions should be minimized.

These factors apply equally to extractive, in-situ, or parametric systems. They apply to systems that are either commercially available or to research systems under development. Cost is always a constraint, but in the field of continuous emission monitoring, cost is not necessarily related to system quality or performance. Evaluations should first be made on a technical basis to determine whether the proposed systems can meet both the regulatory and technical criteria. Costs should then be normalized between those acceptable options so that cost comparisons are made between equivalently performing systems (Brown, 1992). Nevertheless, some risk will be associated with applying existing or innovative techniques to monitoring non-criteria pollutants. If the technique is inappropriate to the application, costs associated with the initial resource investment and noncompliance with monitoring requirements must be considered. These issues will be discussed in more detail later in the chapter.

The selection of a monitoring system should be conducted in a systematic manner (Kopecky, 1979), following established project management procedures in place at the company. Although these procedures may differ from company to company, typical CEM evaluation programs follow approximately ten basic steps. These steps are:

1) Defining the project scope
2) Reviewing the regulations and process requirements
3) Assessing the site
4) Reviewing monitoring options
5) Evaluating vendor options
6) Preparing and transmitting a request for proposal
7) Reviewing bids and awarding contracts
8) Installing the system
9) Approving (certifying) the system
10) Implementing a QA/QC program and operating the system

An example flow diagram that incorporates these steps is given in Figure 6-1.

This process can be lengthy. One author estimated that a typical CEM project will take approximately 40 weeks from inception to certification (Passmore, 1991). Each of these steps will be discussed in detail in the following sections.

6.1 Defining the Project Scope

A CEM project most commonly begins with the assignment of a project manager, usually a project engineer, to develop a technical specification for the

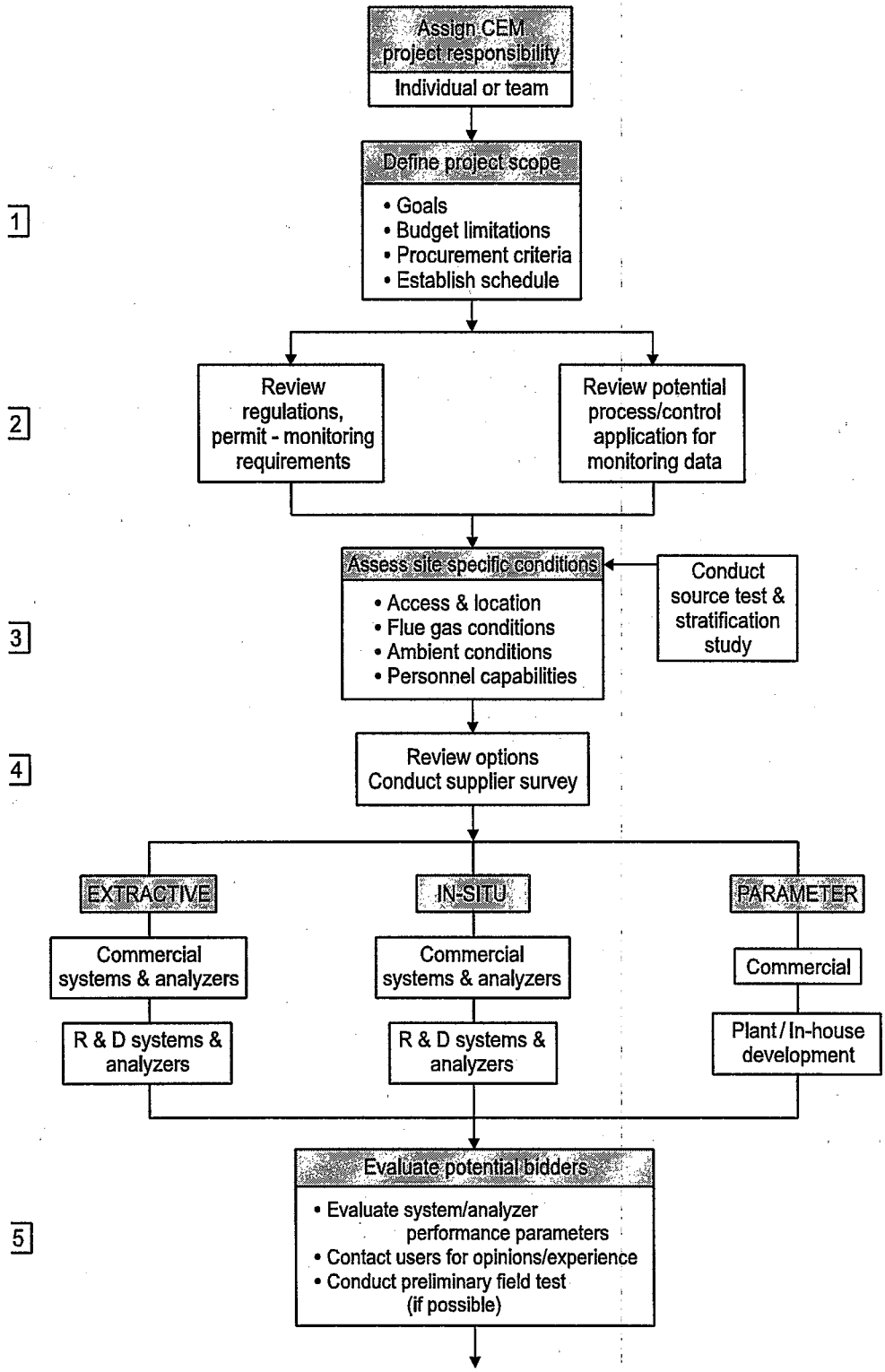

Figure 6-1. Example flow diagram for CEM system selection and implementation.

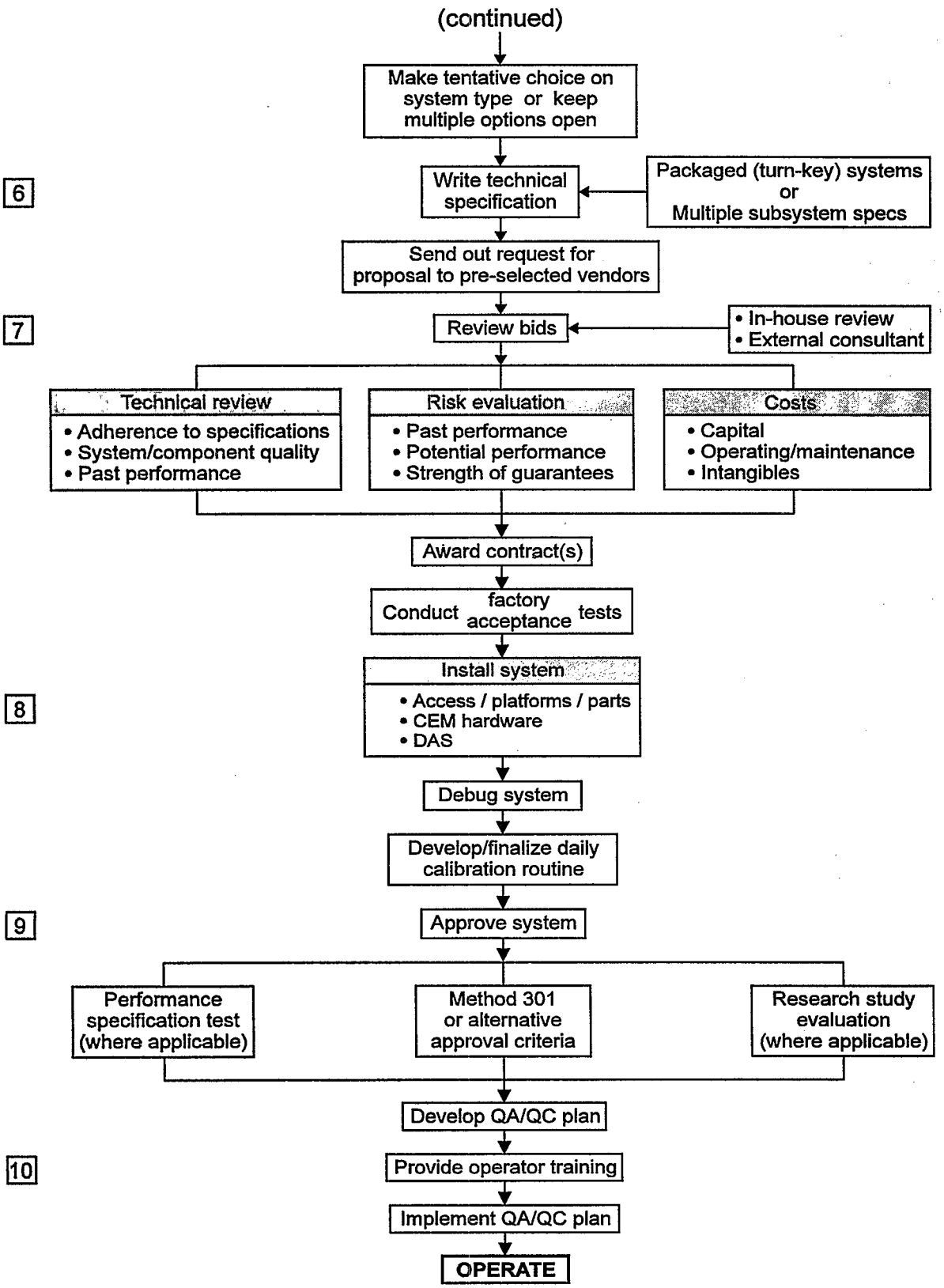

Figure 6-1. Continued

proposed system. Today, most project managers will assemble a team to assist in reviewing regulations and technology, preparing the technical specification, and evaluating the bids received. Instrumentation and control supervisors, technicians, and other plant personnel can be invaluable contributors to this process. The team should also include purchasing personnel, environmental personnel, and, where necessary, legal counsel.

The project scope should be defined at an initial meeting. In this meeting, a decision should be made whether the CEM system will be used solely to meet agency requirements or if it also will be used as input for plant operations control. The implementing rules, the required pollutant measurements, and the data acquisition and reporting requirements should be discussed so that the project team will have an understanding of the purposes of the project. The project manager should have gained enough initial understanding of source monitoring options so that the advantages and disadvantages of extractive, in-situ, or parameter monitoring can be discussed. The estimated budget and procurement criteria as well as the project schedule also should be discussed at this time.

6.2 Reviewing the Regulations and the Process

After the planning stage, the monitoring regulations should be reviewed in detail. This is important to establish the system design criteria for the technical specification. Particular points to focus on are:

- Monitors required, based on how the data are to be reported (see Appendix E of this manual).
- Are parameter surrogate or predictive systems allowed?
- Are time-shared systems allowed?
- Daily calibration techniques allowed (e.g., are Protocol 1 cylinder gases required or are reference spectra or gas cells allowed?).
- Instrument span (range) requirements.
- Sampling, analyzing, and recording frequencies.
- Drift, relative accuracy, and availability requirements.
- Recording and reporting requirements

The requirement for a CEM system may have come through a permit, a state rule, or a federal rule. In some cases more than one rule may require a CEM system. Conflicts between specifications may arise from multiple monitoring requirements. Such conflicts should be resolved with the regulating agency before preparing the request for proposal. Also, many states have developed CEM guideline documents (Nazzaro, 1986, Seidman, 1990). These incorporate essentially de-facto requirements that are often referenced to in the permit. The state should be contacted early in the project to determine if such guidelines have been published and if they must be met by the installed system.

The applicability of a CEM system to both monitor process operations and to provide data for operations control should also be investigated at this time. For example, many companies are now using NO_x monitoring data to allow operators to adjust load in accordance with the plant NO_x control program. VOC monitors may be used to track the efficiency of a catalytic convertor or to monitor loss of product in process operations. Predictive emission monitoring systems have proven extremely useful to monitor; and control many chemical process operations often the regulatory emissions data are merely an extra benefit from the model. However, one must be careful in designing a system for both regulatory and process application. The process monitoring requirements may be either more or less stringent than the regulatory requirements and finding a system to satisfy both at reasonable cost may be difficult.

6.3 Assessing the Site

The plant site and flue gas characteristics should be reviewed next. A suitable location for the CEM system already may have been identified; however, its advantages and disadvantages should be examined carefully. The EPA has established siting criteria for monitoring systems that are very flexible (USEPA, 1996). The intended location(s) should be evaluated for the following:

- Can a representative sample or measurement of the actual flue gas emissions be obtained at the location?
- Is the site accessible?
- Are ambient and physical conditions at the site suitable for monitoring instrumentation?

Sample representativeness is often the biggest issue in monitor siting (EPRI, 1993, Jahnke, 1994). One problem is that flue gas can be stratified, having high and low pollutant concentrations over different areas of the measurement cross-section. Another problem is the presence of non-parallel or swirling (cyclonic) flow, which affects the measurement of flue gas velocity. These problems can be identified by conducting a stratification study, measuring gas concentrations and flow angles over the cross-section at the tentative monitoring location. If the gas is found to be stratified and the location is still viewed as the best available, sampling options will be affected. In-situ path monitors or multiple point sampling systems may be necessary to obtain averaged measurements over the cross-section (Jahnke, 1994).

Flue gas characteristics should be either measured or estimated. This information may be obtained from prior stack test reports and/or from process data. Particularly important for the instrument vendor and the system design are:

- Flue gas temperature and static pressure
- Pollutant gas concentrations (average and range during upset, or other conditions)
- Moisture percentage/presence of water droplets
- Particulate loading and particulate or precipitate carry-over at upset conditions
- Flue gas velocity

Hot metal stacks or flues, excessive vibration, weeping brick stacks after wet scrubbers, should also be noted.

Ambient conditions at the candidate locations should be evaluated. The effects of cold or hot weather, pressure variation at high elevations, sunlight, lightning, entrained dust, or duct gas leaks or stack down-wash on exposed instrumentation and probes should be examined. These issues are critical in the continuing performance of in-situ systems, but can be less of a problem for extractive system instrumentation housed in environmentally controlled shelters.

Another factor that should be considered in the choice of systems is the manpower capability at the facility. Personnel will be required to perform preventive and corrective maintenance on the system after it is certified. Manpower at appropriate skill levels must be available to meet these maintenance demands if high system availability is to be achieved.

6.4 Reviewing Monitoring Options

Sufficient information should be available by this part of the process to begin an evaluation of the various monitoring options. One of the first decision points will be whether to focus on extractive, in-situ, or parameter monitoring systems. Each has its own advantages and disadvantages - again, one must remember that the evaluation should concentrate on determining the best system for the application. This chapter contains guidance for that evaluation, providing flow charts and comments on the application specific features of various systems designs. However, many exceptions also exist. Due to the practically infinite permutations between process units, control devices, flue gas characteristics, and personnel resources, no fool-proof scheme can be developed for monitor selection. In the end, the merits of each option must be considered in terms of the application.

In general, extractive systems provide the most options and are the most flexible in meeting sampling challenges, particularly for HAPs monitoring. In-situ systems can provide low maintenance options when only a few target compounds are required to be monitored. Parameter monitoring systems can offer both monitoring and process control capabilities. For these or other reasons, decision makers may have an initial interest in one type of system over another. Upon further examination, a first preference may not lead to a system suitable in meeting the project goals. The following sections contain flow diagrams that can aid in determining the suitability of various options.

6.4.1 Extractive Systems

Extractive monitoring is the most developed of the three monitoring techniques. It can be a "brute-force" approach to monitoring in the sense that extractive system components can be modified or replaced until some combination of hardware and operating conditions is found that can deliver a viable sample to an analyzer. This is where most HAPs monitoring development programs start. As more experience is gained in extracting and measuring specific compounds, the systems may be simplified.

Figure 6-2 is an example flow diagram for selecting between the various extractive system options.

6.4.1.1 Basic Issues

In the first gate for entry into extractive systems, one should consider three basic issues. If an interest exists in time-sharing one set of analyzers among

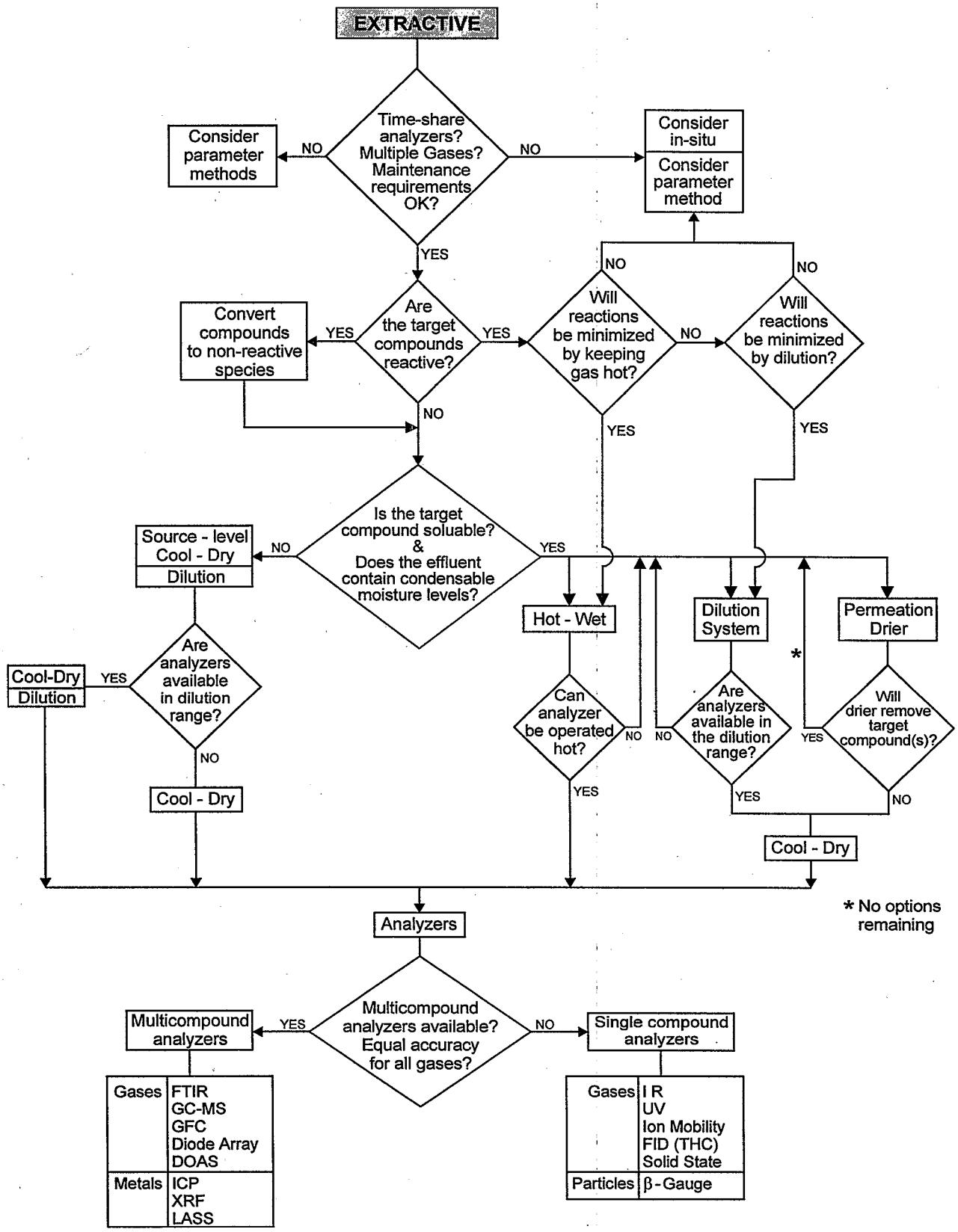

Figure 6-2. Selection considerations for extractive systems.

several units, extractive systems, not in-situ, are appropriate. If the user requires or desires to monitor several gas species, more multi-gas analyzers are available commercially for extractive systems than for in-situ systems. Lastly, extractive systems require more maintenance than either in-situ or parametric systems. These basic issues should be considered when choosing the system. A summary of other technical issues discussed in more detail in Chapter 3 follows.

6.4.1.2 Reactive Gases/Condensable Gases

The tendency of target gases to react or decompose before analysis is a primary consideration when selecting a monitoring approach. Two gases may coexist in the flue gas, but when extracted and cooled they may react. The resultant compounds may not be representative of the target pollutants and, in some cases, may form a precipitate that plugs the system. An organic compound may react with the oxygen in the dilution air of a dilution system, or a compound may catalytically decompose on the probe, tubing, or pump surfaces. Other compounds may be unstable and decompose merely on standing. Where the sampling system perturbs the gases or particles being measured, a representative sample may not be obtained and other monitoring techniques may need to be considered.

The next consideration should be whether the gases being measured are condensable or soluble. Gases like hydrochloric acid, ammonia, formaldehyde, and methanol will drop out along with water in any chiller of a dry-extractive system. Other gases with varying water solubilities may be partially lost to the condensate. If the gases are not condensable, a dry-extractive system would offer a greater range of options in selecting analytical techniques. Of course, dilution systems can be used for non-condensable gases, but the choice of analyzers may be limited to those that are sensitive enough to measure at the lower, diluted concentrations. If the gases are condensable, hot-wet source level systems, permeation dryers, or dilution systems can be used. Dilution systems are preferable here if analytical techniques are available at low ranges. Hot-wet systems require greater maintenance, since parts and materials degrade faster at elevated temperatures. Nafion permeation driers will lose some polar compounds such as ammonia, alcohols, and organic acids, but are acceptable for others, such as the halogenic acids, inorganic acids, and aldehydes (1995, Permapure).

6.4.1.3 Multi-gas vs Dedicated Analyzers and Analytical Methods

The next decision addresses the type of analytical system to be used. If a number of gas species are to be analyzed, multi-component analyzers such as gas-chromatographs, gas chromatography coupled with mass spectrometry (GCMS), or FTIRs may be considered. However, one should evaluate the sensitivity of the analyzer to each of the species analyzed. The analyzer may be able to measure one gas to a 1 ppm level, but other gases only to a 10 ppm level. A separate analyzer may be required to measure the diluent gases (O_2 or CO_2) since the percent level concentrations of these gases may not be consistent with the lower ranges necessary for the pollutant gases.

Caution is warranted when selecting multi-component analyzers. The analyzer previously may not have been applied to a similar process or to a flue gas with similar characteristics. In such cases, the CEM project may not be straightforward and may require some initial research and development work.

Multi-component analyzers utilize techniques such as Fourier transform infrared spectroscopy, GCMS, differential optical absorption spectroscopy, and gas filter correlation (for a limited range of pollutants) for monitoring organic compounds. For metals monitoring, inductively coupled plasma, x-ray fluorescence, and laser spark spectroscopic techniques are under development.

Single component analyzers employ electro-optical, electro-chemical, and other techniques. Differential optical absorption, ion-mobility spectroscopy, fluorescence spectroscopy, and electrochemical methods typically are used. Flame ionization detectors monitor total hydrocarbons, beta gauges can measure the flue gas particulate loading.

If multi-component analyzers are not available, or if single component monitors with better applications experience are found on the commercial market, a collection of single component analyzers may be more appropriate. Single component analyzers are, in general, optimized for that component and may offer greater sensitivity and interference rejection than can multicomponent systems. Unfortunately, very few single-component analyzers have been developed for monitoring air toxics or HAPs. Not that they could not be developed, but the commercial market is small and instrument manufacturers usually do not make analyzers that have no market.

The analytical techniques have been discussed in greater detail in Chapter 3 of this handbook. At this point, an extension of the flow chart is difficult since many factors are involved in choosing the analytical method. One must evaluate the instrument response time, drift, and precision specifications, interference rejection capability, stage of development, ruggedness, cost, and so on. Some familiarity must be gained with the technologies used to monitor toxic gases and Chapter 3 should be reviewed.

6.4.2 In-situ Systems

In-situ systems were developed as an alternative to extractive systems where maintenance levels became unacceptable. Plugging, leaks, and corrosion eventually will occur in even the best designed extractive system, but often these problems can be avoided if the gas is measured without extracting it in the first place. In-situ instruments that require only 50 to 60 hrs of preventive maintenance a year are available commercially (Karpinsky, 1995). Unfortunately, at this point, these instruments have been developed primarily for the monitoring of criteria pollutants. Therefore, the first question that must be asked is whether an analyzer has been developed that can measure the pollutants of interest. Figure 6-3 is an example flow diagram that illustrates points to be considered for decision-making for in-situ systems.

6.4.2.1 Siting Considerations

If a pollutant can be monitored by the in-situ technique, some site specific questions need to be addressed before proceeding. The first and most obvious question is whether an interest exists in timesharing the system between multiple ducts or stacks. If so, go back to extractive systems. Timesharing a spectrometer might be feasible in path systems using fiber-optic cables, but no known applications of this technique exist. Other barriers to the use of in-situ systems pertain to the capability of the monitor to operate at the chosen duct or stack location.

Siting for in-situ systems is important since limits to environmental conditions are encountered that even the best of systems cannot withstand. Exposure to temperature extremes may limit an instrument's application. Although the instrument may have an internal heater to maintain temperature if it gets too cold, the instrument may not have an internal cooler to reduce the temperature if it gets too hot. Lightning can be a problem. An exposed in-situ monitor mid-way up a stack makes an excellent lightning rod. Excessive vibration also may be a problem. This factor often is pointed out as a disadvantage in in-situ systems, however, techniques have been developed to minimize both the effects of vibration and lightning on in-situ instrument systems.

Flue gas characteristics certainly limit the application of in-situ systems. High gas temperatures (>500 °F) affect molecular infrared light absorption characteristics. Hot-metal stacks will emit infrared radiation and reduce the sensitivity of in-situ infrared analyzers. In addition, cycling stack temperatures can distort untempered probes, or cause misalignments in poorly designed path systems. Electro-optical in-situ analyzers require a certain amount of light to reach the detector after it traverses its optical path in the stack. If particulate levels are high, or if high levels of water droplets or other aerosols are present, the intensity of the light may be too weak to afford good signal to noise levels. Opacity levels common to most flue gas exhausts (<20% opacity) do not present a problem for most in-situ monitoring applications.

The monitoring location for the in-situ system must be accessible. Duct or stack locations accessible by catwalks or stairs are ideal. Systems located in the annulus between chimney and flue and accessible by man-lift have traditionally been preferred but may now require confined space entrance permits due to OSHA regulations. Sites accessible only by ladder, requiring a safety harness, are not ideal. The rule-of-thumb is: if no one is willing to go up and service the system in the middle of winter, find another location or purchase some other system.

6.4.2.2 Flue Gas Stratification Issues

Flue gas stratification can be a major problem in obtaining representative flue gas measurements. Stratification is the uneven distribution of pollutant, diluent, or particulate concentrations over the area of the sampling cross-section. Air in-leakage, combining ductwork, mixing or combining effluent streams, duct geometry, and flue gas physical properties can cause pollutants in the gas to stratify. The flue gas velocity can also vary over this cross-section; in the case of non-parallel cyclonic (swirling flow), its direction can vary also. Cyclonic flow presents one of the most challenging sampling problems. Selecting an alternate sampling site is usually more prudent than attempting to measure flow under cyclonic conditions.

Three approaches can be taken to minimize stratification effects. One is to install a path in-situ system, where a measurement is made on a line across the stack. The measurement represents a line average, not an area average, but the average measurement

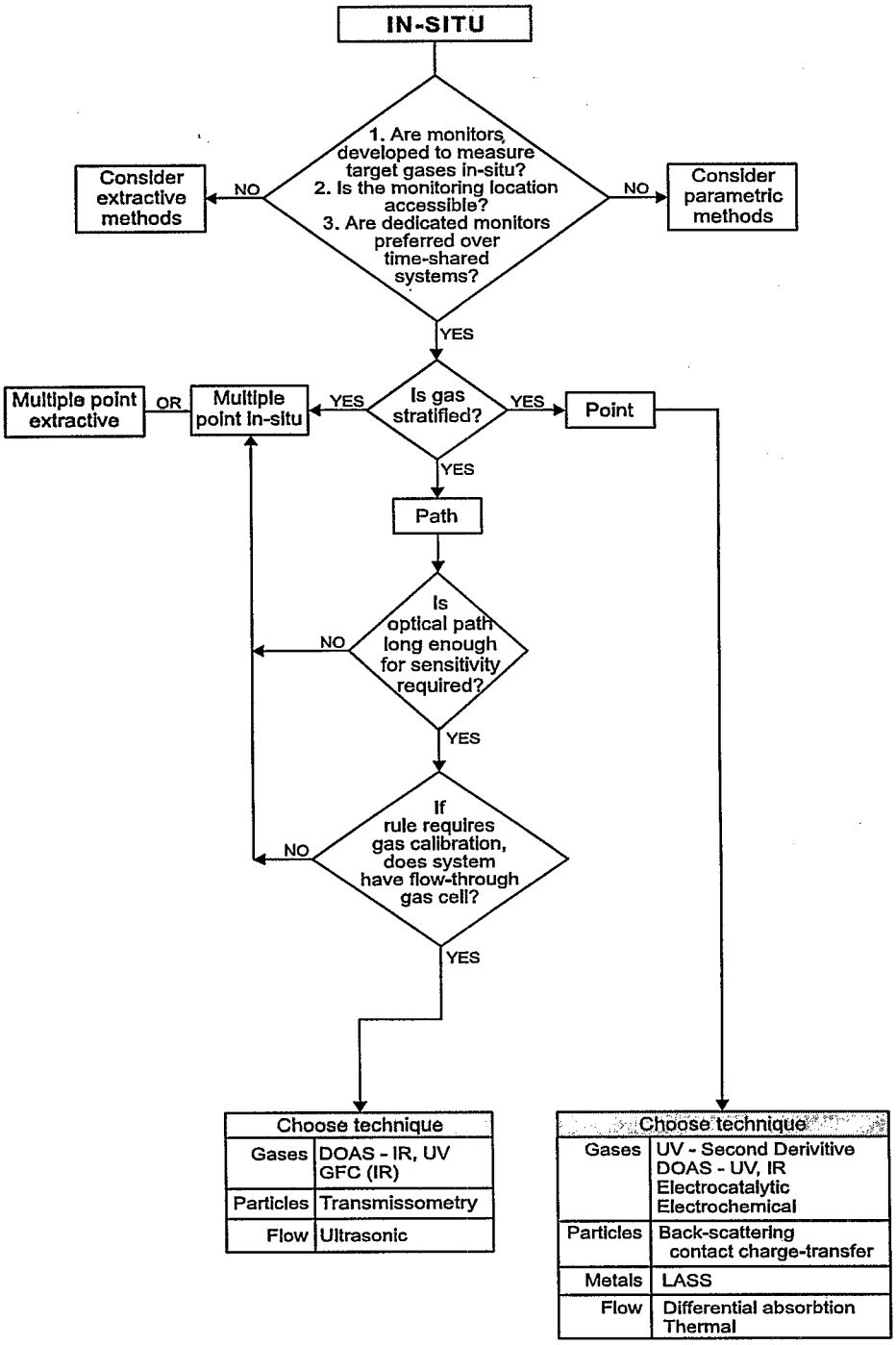

Figure 6-3. Selection considerations for in-situ systems.

can be more representative than a single point measurement under varying stratification conditions.

Another approach is to use multiple probes or monitors to sample at several points on the cross-section. This technique has been used in monitoring stratified flow in ductwork by placing a grid of thermal sensors at measurement points defined by EPA Method 2. Sometimes, increasing the number of sampling points from one to just two or three can greatly improve the representativeness of the measurement.

In situations where the stratification pattern is stable over varying process load or operating conditions, a single point in-situ monitor or extractive system probe may be suitable if a point representing the average cross-sectional concentration or velocity can be found. Detailed solutions to these problems are treated elsewhere (Jahnke, 1994 Chapter 2 and references therein).

6.4.2.3 Path In-situ Monitor Considerations

If the decision-making process has led this far to path in-situ monitors, two other factors must be considered. First, for small diameter ducts or stacks, the sensitivity of the instrument may be limited. At low concentrations and short pathlengths, too few pollutant molecules will be present to absorb much light energy. The instrument detector may not be sensitive enough to see very small changes in the returning light energy and the sensitivity of the instrument will suffer. Longer path-length options might be considered, such as measuring across the stack at an angle (Reuter-Stokes, 1995), measuring lengthwise down the duct or stack, or even pulling the flue gas into a longer by-pass tube to make a hybrid in-situ/extractive system.

The second important issue regarding path in-situ systems is a regulatory one. In the United States, many CEM regulations require the use of calibration gases for daily calibration (see for example, 40 CFR 75 Appendix B). This has been addressed in path in-situ systems by using a flow-through gas cell (Carman, 1993). Problems do arise when certified standards are not available or are not available at appropriate concentrations. Other means for performing calibration checks have been developed that use reference spectra or sealed gas cells containing pollutant gases of known concentration. These techniques are used commonly in European instrumentation and are accepted by the European Community. The use of reference spectra is convenient, especially for monitoring air toxic compounds where reliable cylinder gas standards are not available. If one desires to use these alternate calibration techniques, the agency should be consulted first.

6.4.2.4 Analytical Methods

The analytical techniques utilized in point and path in-situ systems are similar to those used in extractive systems, although the number of applicable techniques is limited due to in-situ system design constraints. Chapter 3 contains detailed discussions of the various techniques.

For in-situ gas monitoring systems, the differential optical absorption spectroscopy offers the greatest flexibility for monitoring air toxic organic compounds. Spectrometer systems, tuned lasers, or various filtering methods that distinguish between different light wavelengths in the IR or UV range have all been employed in path monitoring systems. Spectrometer systems offer the advantage of monitoring a number of compounds simultaneously. Tuned lasers, optical filters, and gas filter correlation techniques are somewhat limited, but still may monitor from 1 to 8 compounds at a time. On the other hand, transmissometry is the only path in-situ monitoring technique available for particulate matter.

More analytical options are available for point in-situ systems. In addition to the electro-optical methods typically used for monitoring gases, electro-analytical methods can be employed as well. Electro-chemical or electrocatalytic sensors can be supported at the tip of a probe for direct, in-situ measurements. Particulate matter may be monitored by the techniques of light scattering and contact charge transfer, whereas metals can be measured in-situ by laser spark spectroscopy. Flow can be monitored by a variety of differential absorption and thermal techniques.

6.4.3 Parameter Monitoring Systems

Parameter monitoring stands as a distinct alternative to the use of sampling and analytical hardware of traditional CEM systems. Parametric techniques offer some distinct advantages, but also suffer some disadvantages that are not overcome easily. These issues are discussed in more detail in Chapter 4 of this manual. Figure 6-4 contains a process for choosing parametric systems when they are required or are being considered as a monitoring option.

The first major decision point associated with parametric systems is whether the permit or regulation allows its application for meeting the monitoring requirement. Parameter surrogate monitoring is specified in a number of the NSPS and may be specified in Title V operating permits. Parameter

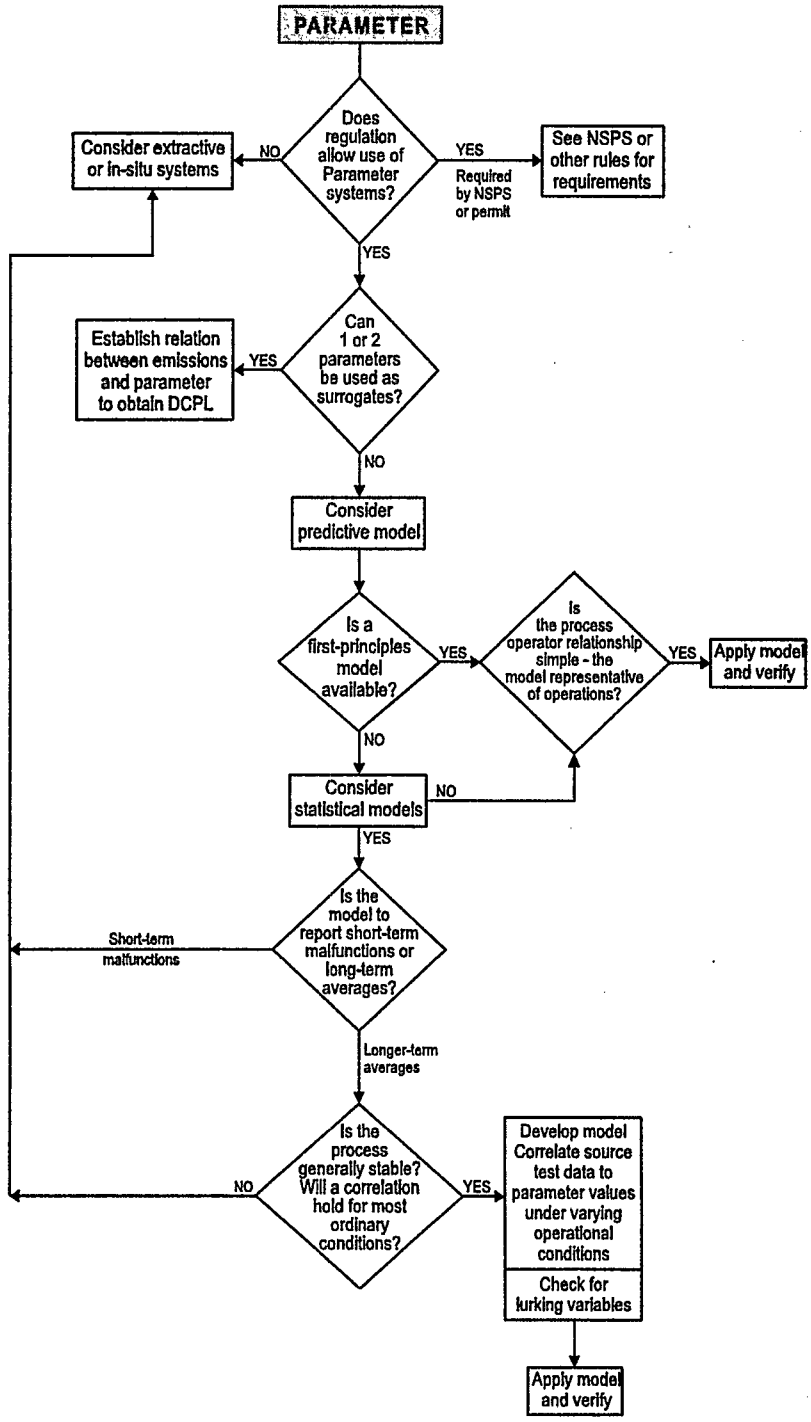

Figure 6-4. Considerations for parameter monitoring systems.

monitoring is also acceptable in the proposed CAM program.

The simplest approach to using operational parameters in emission monitoring is as a surrogate for the actual emissions. If a clear relationship can be established between emissions and one or two parameters such as pressure drop, temperature, etc., a parameter value (the DCPL - direct compliance parameter limit) may be acceptable as a de facto emissions standard. If this is not acceptable in meeting agency requirements, then a predictive model may be developed.

As discussed in Chapter 4, two types of predictive models are used: the first principles or phenomenological models and statistical models. Both models may provide additional insights into process operations. Models should be tested and verified. If they fail verification, one may always return to CEM analytical hardware.

Simple statistical models can be developed in-plant, by consultants, or companies that specialize in their development. If the model is to be used for compliance with short term emission exceedances, excessive correlation testing may be required to model all the conditions under which an exceedance might occur. This testing may be very difficult to perform or prohibitively expensive. If, however, longer term averages are to be reported or the data will be used to report adherence to emission limitations, the model may not have to be as robust.

The statistical model should be developed under varying operating conditions and also evaluated for the effects of parameters or conditions not included in the model. The final model should be robust, having an accurate solution for each set of operating conditions. Models can cross-check themselves, but all models should be re-verified periodically.

6.4.4 New Market Products and Systems under Research and Development

Figures 6-2 and 6-3 are flow diagrams for evaluating monitoring approaches that are, in general, commercially available, or where some previous similar experience exists in their application. In evaluating new market products or newly developed techniques, following such a diagram may be difficult if little is known about the system limitations. For such new systems, an alternative flow diagram is suggested, Figure 6-5.

In this approach, the pollutant properties are considered first, the analyzer capabilities are evaluated, and then the sampling system options are reviewed. This evaluation approach proceeds from the analyzer to system selection rather than the approach given in Figures 6-2 and 6-3, from the system type to the available analyzers.

6.5 Evaluating Potential Bidders

After the site characteristics and monitoring options have been evaluated, information should be obtained on potential suppliers and bidders for the project. Potential bidders may include CEM system integrators, instrument manufacturers, data acquisition system (DAS) vendors, computer software firms, and environmental consulting/contracting companies. Many of these companies will exhibit at trade shows and advertise in trade journals. Lists of instrumentation companies and CEM system integrators are given in trade journal "Buyer's Guides," but these lists generally are not very discriminating.

Once contacted, vendors will send literature, call, visit, and market. Although marketing calls may seem onerous, they can provide a means for assessing both the applicability of the vendor's approach and the capabilities of the vendor. On the other hand, the vendor who understands the requirements and limitations early in the proposal process, can deliver a better product in the end.

At this point in the monitoring system selection process, the project manager and team should concentrate on screening the assembled list of potential vendors to those that meet project selection criteria (Brown, 1992). These initial criteria should include an evaluation of:

- System capability in meeting regulatory requirements
- System capability in meeting plant process/control needs
- Suitability of the system for operation at the plant, at the intended location, and under plant operating conditions.

Contractual requirements such as bid bonds, warranties, guarantees, and other commercial aspects should be discussed before a formal bid solicitation. Preliminary cost estimates, maintenance costs, and vendor service capabilities also may be important screening issues.

To help in this part of the process, the team should contact other users of monitoring systems, preferably users in the same or similar industries. Here, the

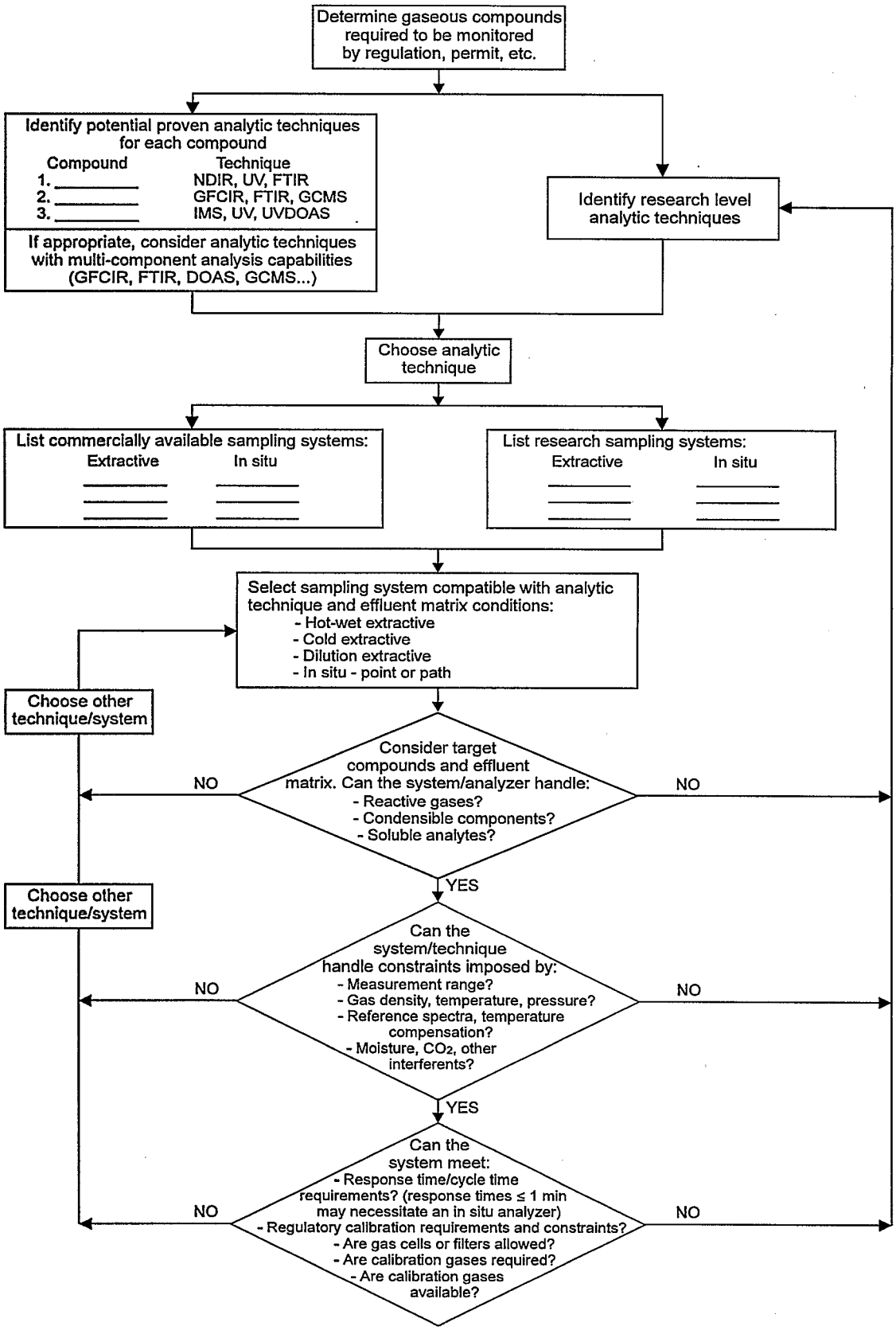

Figure 6-5. Alternative approach to monitoring system decision-making.

industry network becomes useful. The opinions and experience of others can be extremely helpful in maintaining objectivity when evaluating the claims of the various suppliers. However, as a cautionary note, be aware that the experience of others is based on specific applications and may not be appropriate to the current project. Industry networks can fool themselves by reaching an overall consensus - everyone agreeing that only one specific approach is the correct approach. A project manager conducting a more objective evaluation may end up in the position of deviating from the "conventional wisdom," and find difficulty in justifying a different, but more appropriate technology to management.

When a corporate office is planning to purchase a number of monitoring systems for company facilities, management often desires to standardize, having one vendor supply identical systems to all of the plants. However, prudence should be shown by first purchasing one system, evaluating the system technically, and evaluating the performance of the vendor in terms of response and service before committing to a corporate-wide purchase. Another approach is to invite vendors to demonstrate equipment during a short-term field trial. A field trial will be particularly appropriate if the source conditions at the trial are similar to those of the intended application. Vendors are becoming hesitant in participating in such programs since they are costly, do not necessarily reflect actual equipment performance, and may offer no return if the system is not selected. However, if an instrument manufacturer has developed a new analytical method or monitoring technique, it must be field demonstrated before it can hope to have any market acceptance. The manufacturer will be eager to obtain the cooperation of a plant to help in proving the system. Many good system applications have resulted from such developmental work.

The screening process should identify at least three, but preferably more, potential bidders. If company policy is to accept the lowest bidder, then only vendors that can provide a product that the plant can live with should be put on the bidder's list. If the company requires that all requesting or potential bidders be included on the list and that no prior discrimination is allowed (as is the case in some municipal facilities), then this entire exercise is useless.

6.6 Writing the Bid Specifications

The purpose of performing an initial vendor screening is to simplify the writing of the technical specification. As a result of the evaluations conducted on the available technologies (Step 4 of this strategy) the project manager may have decided initially to focus on extractive or in-situ systems. However, a vendor may have later pointed out the merits of predictive monitoring systems. Options still can be kept open in the technical specification by incorporating a set of uniform criteria that either technique can satisfy.

After a consensus has been reached by the CEM project team, a detailed technical specification can be prepared. In most cases, the team will not have to start from ground zero and develop an original document since model and example specifications are often available. The Electric Power Research Institute has developed a model Request for Proposal package for CEM systems required under 40 CFR 75, the acid rain program (EPRI, 1993). The package includes an example transmittal letter, suggested terms and conditions, and a guideline technical specification. The package can be modified easily for other monitoring programs and serves as a good starting point. Technical specifications also tend to circulate within the networks of a given industry and technical specification packages frequently can be "borrowed" from someone else. Vendors also offer bid packages to "assist" potential clients in their monitoring programs. However, these packages are usually self-serving, being written in a manner to exclude competing technology or competitors. The company itself may have standard specification requirements and the monitoring specification may have to be tailored to meet the criteria of the contracts department. Whichever route is chosen, the specification should provide a basis for the purchaser to obtain the system desired and a basis for legal action if it is not satisfactory after installation.

A typical CEM system specification incorporates the following (from Jahnke, 1993):

1) Purpose. A brief statement of where the CEM system will be installed, the number of units that will be monitored, and statement of the regulatory requirements applicable to the installation.

2) Scope of Work. An outline of hardware, software, and services to be provided by the vendor. This section may include a basic system configuration, list of the number of analyzers required, data acquisition/control requirements, and may specify brand-names of analyzers or components if desired. Vendor furnished services may include complete system engineering, installation, and start-up, if desired.

3) Equipment and Services Provided by Others. A listing of equipment and services that the vendor is not expected to supply. This may include

equipment or supplies such as elevators, ports, catwalks, platforms, electrical supplies, foundations, or calibration gases. Services supplied by plant personnel or others may include system installation, wiring, or certification.

4) Description of Operating Conditions. A description of environmental and stack gas conditions at the sampling locations. Diagrams of sampling ports and access conditions should be provided here or referred from here to the appendix of the specification. Flue gas characteristics such as moisture content, velocity, and temperature, and the expected composition and concentrations of pollutants in the flue gas should be supplied. This information is critical to the vendor for the design of the system.

5) Design Criteria and Construction. A detailed description of the system on which the bid is to be prepared. The intent is not to provide all design data, but to provide the vendor with an understanding of the system requirements from both regulatory and operational aspects. Design requirements include adherence to standards, codes, and regulations. They also include specifications for instrument range, drift, and response time. They may include specifications for sample conditioning, interfacing with other plant systems, and data acquisition requirements and reporting formats.

   This section will constitute the bulk of the specification. However, care must be taken not to "over-specify" the system. The vendor must be allowed leeway in the design to use his own experience in CEM systems for the job. If the requirements are too stringent, either no one will bid on the system or they will be ignored in the systems offered.

6) Vendor Furnished Services. A listing and description of services desired from the vendor. These may include, total project management, installation, training, performance testing, or on-going maintenance services.

7) Inspection and Testing. A listing of certification guarantees and warranties expected from vendor. These may include factory checkout and certification provisions, performance specification test guarantees, and system availability requirements.

8) Equipment Delivery Requirements. A statement of progress report requirements, delivery dates, and shipping requirements.

9) Engineering Data and Documentation. A listing of required system documentation. This should include accurate system schematics and wiring diagrams, operating manuals, maintenance instructions, and DAS operating instructions and documentation.

Separate technical specifications may be written for various subsystems. Frequently, a separate specification is written for the data acquisition and handling system. Special precautions are necessary to ensure that the two systems are fully compatible (see Chapter 5).

Services such as training, maintenance, and performance testing should be requested to be bid separately as options. Costs for these services should also be bid separately since they tend to be quite variable between bidders. Separating services from the system technical specifications will assist in the evaluation process and will offer more flexibility in subsequent negotiations.

A set of technical specifications normally will be accompanied by a set of "Standard Terms and Conditions" prepared by the company contracts department. This document will include legal requirements for insurance, limits of liability, remedies, disputes, etc.

After a draft bid package has been prepared, it should be circulated to other departments within the company before it is released (Brown, 1992). Legal departments, computer systems, purchasing, and various engineering departments may wish to provide input or comment on areas of their particular concern. The package should then be revised appropriately, finalized and issued. If not already having done so, bidders should be allowed the opportunity to visit the site and observe plant conditions and operations to better design a proposed system. Approximately four weeks should be allowed for bidders to respond to the Request for Proposal.

6.7 Reviewing the Proposals and Making a Decision

Reviewing proposals objectively is difficult since, by the time proposals are received, members of the CEM team will have some preconceived idea about what will be the "best" system or who will be the "best" vendor. However, the decision should be based on a systematic evaluation of the proposal following objective criteria established before the RFP, keeping in mind that the quality of the proposal will often be indicative of the quality of the work.

6.7.1 Areas for Review

Three principle areas need to be reviewed on a preliminary basis after receipt of the proposals (Figure 6-6).

These areas include a technical review, an evaluation of risk (especially for new systems for new applications), and cost. This review is preliminary because, despite all good intentions in drafting clear, concise, and explicit technical specifications, one vendor will offer oranges and another will offer apples. One usually must obtain further information, clarify exceptions, and normalize equipment costs and services to make valid comparisons.

6.7.1.1 Technical Evaluation

In the technical review, a determination should be made whether the system will meet all regulatory specifications and any additional specifications given for the plant application. Most proposals will state that all specifications are met; however, corroborating information should be provided so that the review team may verify such statements.

Technical Review
Adherence to Technical Specs.
System/Component Quality
Proposal Quality
Risk Evaluation
Past Performance
Potential Performance
Strength of Guarantees
Costs
Capital
Maintenance
Intangibles

Figure 6-6. Areas for proposal review.

The system and component quality should be evaluated. A proper evaluation here may require prior knowledge on the part of the team members, or a reliance on the experience of others who have purchased similar systems or instrumentation. System quality may be difficult to evaluate for newly developed analyzers. The frequent lack of experience of entrepreneurial instrumentation companies in stack monitoring applications is a factor that must be considered in the review.

The best proposals are those that are written specifically for the plant application. The worst consist of a price quote and a collection of vendor trade literature. Most proposals will fall somewhere in between these extremes, generally towards the lower end of quality. Not that better proposals can't be written, but when a vendor sales or project manager has to respond to numerous proposals, few receive the attention that is desired. However, if a vendor really wants the job, enough care and time will be put into the proposal to show that a good system can be provided for the application. Ultimately, well-prepared proposals have greater success in being awarded.

6.7.1.2 Risk Evaluation

The evaluation of risk in a CEM program is not simple. Frequently, the results of important decisions are not known until much later in the implementation of a monitoring program. An untested assumption or a faulty decision early in the development of a monitoring program may affect many subsequent steps. The project manager must recognize the risk associated with critical decisions and understand the impact of unfavorable outcomes on both the immediate task and subsequent activities.

The primary risk associated with selection of a monitoring approach or specific equipment is that the selected system will not perform acceptably. When a general failure occurs, the investment of resources (time for internal personnel, subcontracted services, and capital expenses) produces neither benefit nor compliance with applicable monitoring requirements. An entire system may need to be replaced or new regulatory requirements may need to be negotiated.

The project manager must focus on the specific issues of the particular monitoring application. Past performance of similar systems may provide a limited basis for evaluation of risk. Contractual conditions, warrantees, and performance guarantees can draw attention to specific issues and may also provide some recourse for the purchaser if performance proves to be unacceptable. However, to minimize risk of unacceptable performance is always better than to rely on the threat of litigation.

Because of the importance of CEM data to source compliance programs, the CEM project manager must consider how inaccurate, imprecise, or non-representative monitoring data affects source operation and control equipment costs. The risks and costs associ-

ated with inaccurate data must be weighed against the cost for more reliable monitoring results. Achieving the appropriate balance between these risks and costs becomes more crucial as emission levels approach the applicable limit. One may expect that a source operating well within the applicable limits will be willing to accept a greater level of uncertainty in the monitoring data. In this case, the source operator may be able to choose more economical alternatives over more accurate data. On the other hand, a source with a minimal compliance margin will place greater value on accurate monitoring data and may be able to justify the greater expense associated with achieving higher levels of performance. Costs associated with modification of process or control equipment and operational costs due to changes in source operation and maintenance practices necessary to meet emission limitations are considered "compliance costs" for the applicable standard. Such costs should not be attributed to the monitoring program. Similarly, the risks associated with non-compliance with emission standards also must be considered separately even though such problems might be detected only by means of the monitoring program.

The proper balance between risk and cost will depend on the monitoring approach and many source-specific factors. This balance must be determined on a case-by-case basis. Two examples of risk evaluation are provided below:

6.7.1.2.1 Example 1 - PEM System Risk Assessment. Consider the selection of a PEM system relative to a conventional CEM system for the measurement of gaseous pollutants. In this approach, hardware expenses are mostly eliminated and the initial capital outlay for the PEM system may approximate the cost of the CEM system DAHS. As compared to the CEM system approach, additional comparative emissions testing is required to develop either the "first principals - phenomenological" PEM system or the "statistical - inferential" PEM system. Thus, an investment occurs in direct costs (i.e., planning and engineering time for company personnel or similar subcontract services by consultants or vendors). PEM system performance tests involving comparisons with independent emissions measurements may be required soon after the model is established. A similar test may have to be repeated on a periodic basis as a QA procedure.

To assess the risk associated with a PEM system approach, estimates must be made of the initial model development cost, initial confirmation performance test cost, and subsequent periodic QA test cost. These are the expected costs that will be incurred in all PEM system applications. In addition, the potential costs associated with unfavorable outcomes must be considered. The likelihood that the PEM system will fail either the initial or subsequent tests and the potential costs of retesting must be assessed. Also, the likelihood that the initial model development effort will need to be repeated either because of repeated failures of performance tests or because of fundamental changes in the fuel, raw materials, process, or control device function must be considered.

The ultimate cost of the PEM system will be very sensitive to the risks discussed in the previous paragraph. The relationship as shown in Figure 6-7 is suggested as a method of estimating the cost of the PEM system.

The consistent application of arbitrary estimates or ranges of the likelihood of various outcomes in the above relationship will assist the decision maker in assessing the overall cost for the PEM system. An example of such an analysis is shown in Figure 6-8. Prudence dictates assigning higher risk factors to industries or applications where little previous experience has accumulated. Higher risk factors should be assigned to applications within agency jurisdictions where strict monitoring regulations or QA requirements may be adopted.

6.7.1.2.2 Example 2 - CEM System Risk Assessment. The likelihood that a CEM system will perform acceptably will depend to a great extent on the pollutants or compounds to be measured. Opacity, SO_2, and NO_x CEM systems are now considered to be very reliable for many applications. However, the development status of CEMS for non-criteria pollutants spans a very wide range. For example, "total hydrocarbon monitors" employing FIDs have been installed at certain sources in the United States for a number of years. CEM systems for Hg are available from several manufacturers, but issues related to calibration standards and reference test method procedures are being resolved. Monitors for other metals (e.g., "multi-metals CEM systems") are beginning to become available commercially. The project manager must recognize that the likelihood of a general failure of the monitoring system to perform acceptably is very significant until commercially available systems are installed and experience is gained at a substantial number of facilities.

For commercially available CEM systems, risks can be minimized by careful consideration of each step in the CEM program implementation. The selection of a CEM measurement location is a key aspect in the development of a monitoring program and is an example of a

$$\$LC(N) = [\$IM + (1 + P_1)\$T_P][1 + P_3 + P_4] + N[M(1 + P_2)\$T_{QA} + \$O\&M] \qquad \text{Equation 6-1}$$

Where:

$\$LC(N)$	=	Lifetime cost for N years
$\$IM$	=	Initial model development cost (including software, hardware, installation, and development test costs)
$\$T_P$	=	Performance test cost
$\$T_{QA}$	=	Periodic quality assurance test cost
$\$O\&M$	=	Annual PEM system operation and maintenance costs (exclusive of periodic quality assurance tests)
N	=	Years of expected operation
M	=	Number of periodic QA tests required per year
P_1	=	Likelihood of performance test failure (range of 0 to 1)
P_2	=	Likelihood of periodic QA test failure (range of 0 to 1)
P_3	=	Likelihood model must be redeveloped because of model failure during expected useful life of PEM system (range of 0 to 1)
P_4	=	Likelihood that a new model must be developed because of fuel, process, or control equipment changes during expected useful life of PEM system (range of 0 to 1)

Figure 6-7. Cost estimation method for PEM system.

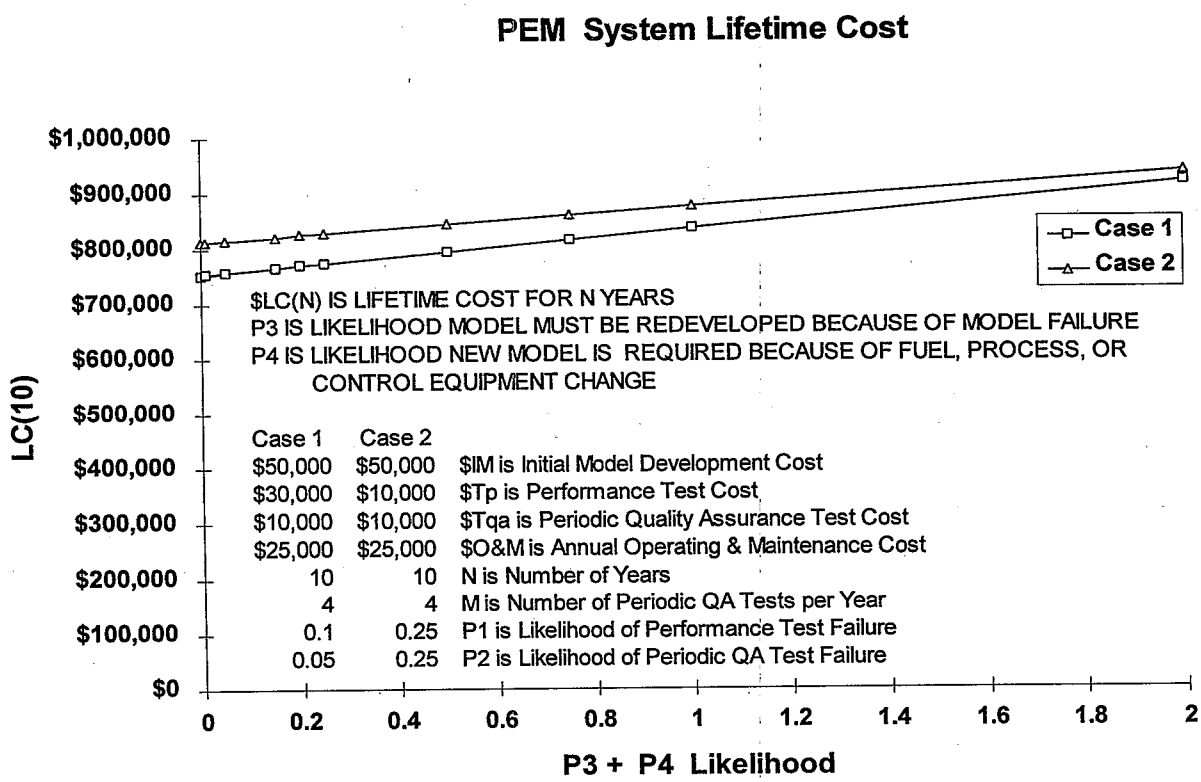

Figure 6-8. Analysis of PEM system lifetime cost for two example cases.

decision that affects many subsequent steps. Selecting a tentative monitoring location early in the planning phase of a monitoring program to specify emission and environmental conditions is very important for potential vendors. Furthermore, the costs for access to the monitoring location (ladders, elevators, platforms, sample ports, etc.) and providing support utilities may be greater than the capital cost for the monitoring equipment. Flue gas (or flow) stratification at a measurement location can affect the representativeness of monitoring data substantially. In evaluating a tentative monitoring location, the following must be considered: 1) the availability of alternate monitoring locations, 2) the cost to relocate a monitor if the tentative location is later found to be unacceptable, 3) the likelihood of pollutant, diluent, or flow stratification at the location and the reliability of indications that it may exist, 4) the likelihood that a failed relative accuracy test would have to be repeated and the costs for retesting, 5) the cost associated with potential delays in the approval process of the CEM system, and 6) the practicality and cost associated with performing a stratification test before finalizing the location selection or prior to performing the relative accuracy test. The risks and costs associated with all of these factors must be balanced during the planning effort.

Assessment of risk for the initial acceptance test and subsequent QA checks and audits is also important. The cost of the initial acceptance test is usually substantial. A well planned and executed test can be a thorough evaluation of CEM system performance and the adequacy of the calibration procedure. A poorly performed test may result in failure to meet specifications, even for the best designed and implemented monitoring program, resulting in a costly retest and substantial delays. A poorly performed test also can allow a flawed CEM system design or improperly applied CEM system to be accepted when it should not. This outcome avoids immediate retesting but leaves the facility with an unreliable monitor. Unfortunately, this situation may continue for many months until the underlying problems are identified by subsequent QA audits or other activities.

In planning the initial and subsequent tests, the following must be balanced: 1) the level of preparation and oversight for the test and the associated costs, 2) the qualifications and capabilities of the test team, 3) the likelihood that the CEM system will fail a test and the cost for retesting, 4) the likelihood that the test will not detect an important performance problem affecting either regulatory requirements or contractual guarantees, and 5) the cost associated with potential delays in the approval process resulting from a failed test.

Other QA risk criteria to consider are: 1) the likelihood or expected frequency of daily drift check failures, 2) likelihood of periodic QA test failures and the need for retests, 3) expected and/or guaranteed CEM availability, 4) availability of replacement parts and service from the vendor, and 5) the supplier's response time to provide service or replacement parts/monitors. These factors will affect the ongoing operating cost for the monitoring program and they will affect the risk associated with satisfying minimum data availability requirements of the regulatory agency.

Evaluating the risks associated with a CEM system or PEM system monitoring program requires the likelihood and impact of unfavorable outcomes of various decisions and events. Considering the downside risks can help to focus attention on the most critical issues and may be helpful in preventing negative possibilities from turning into actual experiences.

6.7.1.3 Cost Evaluation

In addition to the initial capital expense for the purchase of a monitoring system, other start-up costs are associated with engineering, selection, purchase, installation, and performance testing of the monitoring system. Recurring or ongoing costs for the operation, maintenance, quality assurance, recordkeeping and reporting associated with the monitoring program also must be considered. The costs that will be incurred at a particular facility will depend on many factors and will differ greatly between facilities. The pollutants to be monitored, the type of monitoring approach selected, the monitor installation location and conditions, and many other source-specific factors will affect the cost of the monitoring program.

All of the costs that may be expected should be taken into account in the cost evaluation of competitive monitoring proposals. In most cases, the majority of costs that will be encountered over the life of the monitoring equipment will not be represented in a monitor equipment vendor's proposal. Many other external and source-specific factors over which the vendor or equipment supplier has little control need to be considered. Nevertheless, all of the expected costs should be projected and considered in conjunction with each vendor's cost proposal and technical approach. This is necessary both 1) to evaluate different proposals on a consistent basis,

and 2) to determine the total cost of the monitoring program for the affected facility. Much experience has shown that the proposal offering the lowest initial purchase price is not necessarily the least cost approach over the CEM program lifetime.

Costs must be evaluated over the useful life of the equipment or on another basis that accounts for both initial and ongoing costs. The average life of a CEM system is likely to vary between five and ten years depending on the type of equipment used and the monitoring application. The distribution of these costs between capital outlays for initial equipment purchases, facility modification costs, software purchases, subcontracted support services, and internal costs for engineering/planning, purchase, operation and maintenance, reporting, recordkeeping, and administrative support will vary for each particular monitoring application. A checklist is provided in Appendix F which may be helpful in evaluating some of these costs. The checklist is offered as a guide to encourage thinking about CEM program costs in a comprehensive manner.

6.7.2 A Matrix Evaluation Technique

A common technique used in evaluating proposals is to prepare a matrix of various evaluation factors and to assign a maximum possible score to each factor. For example, each listed item in Figure 6-6 could be used as an evaluation criteria and assigned a maximum score of 10. The matrix would then be composed of 9 criteria evaluated for each proposal received (Figure 6-9).

Each returned proposal is scored and the total scores for each category (technical, risk, cost) are obtained. Each member of the evaluation team should complete the matrices for each vendor independently. Then, they should meet as a committee and reach a scoring consensus on each evaluation criteria. Each member should justify his or her score until agreement is reached. The use of an outside consultant or CEM expert from another company to provide an independent, objective review of the proposals also may be helpful.

6.7.3 Normalizing the Issues

The proposal review may identify the best system for the application, but frequently many questions and issues are raised that require clarification. One vendor may have drawn exception to numerous specifications, whereas another may have agreed to all of the specifications. Another may have proposed an inferior conditioning system, but a superior analyzer. A service contract of one may have proposed 12 trips in a year including expenses,

	BID 1	BID 2	BID 3	BID 4
TECHNICAL REVIEW				
• Adherence to Technical Specs.				
• System/Component Quality				
• Proposal Quality				
RISK EVALUATION				
• Past Performance				
• Potential Performance				
• Strength of Guarantees				
COSTS				
• Capital				
• Maintenance				
• Intangibles				

Figure 6-9. Simplified example matrix evaluation.

whereas another offered 8 trips plus expenses. Another may have a superior system but misunderstood the data acquisition system criteria. Often, another round of evaluation will be necessary to bring the proposals to a stage where they can be compared on a uniform basis. This can be achieved by listing all exceptions and questions and requiring a response from the vendor suitable for review within one to two weeks. For large projects, bringing the vendors to the plant to review their proposals and clarify outstanding issues may be necessary.

All costs should be normalized so that equivalently performing systems would be purchased for the stated quotations. Some costs may have to be adjusted up or down if equivalent services are not offered by the vendors. Intangible issues also need to be considered and factored into the risk rankings. These intangibles include an assessment of the stability of the company (its ability to provide parts and service five years or ten years from the equipment purchase), its ability to honor guarantees, the likelihood of the company being sold, the probability of the only person who knows anything leaving, etc.

By this time, the project team should have determined which proposals are technically acceptable and have ranked the proposal costs. Depending upon company policy or pre-established guidelines, a contract may be awarded to the lowest bidder of those technically acceptable, or technical/cost considerations may be weighted. For example, the project team may agree initially that technical factors will contribute 80% in the final evaluation and costs 20%, or vice versa. On the other hand, after all this analysis has been done, it may be thrown out and the award decision based on subjective opinions that a favored vendor is the only vendor that can develop a successful operating system for the application. If the latter approach is taken, company resources have been wasted.

An evaluation can be objective and systematic, or subjective. An ostensibly systematic evaluation can also be distorted and biased to achieve a desired end. However the decision is made, the company must understand that plant managers, plant engineers, and technicians will have to work with the system for many years into the future. The choice of systems will be considered a good choice for all concerned if it meets the three criteria discussed in the introduction to this chapter:

1) The design meets regulatory requirements and is consistent with plant operating requirements.

2) The materials, components, and techniques are reliable and durable under the constraints of ambient and flue gas conditions, and operating conditions.

3) The system is easy to use, serviceable, and cost-effective in its long term operation.

6.8 Installing the System

After the contract is awarded, construction will begin on the system. This will take several months, depending upon parts availability and the vendor's backlog. Few vendors have systems that can be provided "off-the-shelf," since most begin construction after receipt of an order. A typical time to fabricate and deliver the CEM system can take from two to four months (Passmore, 1991, Ferguson, 1991, Retis, 1992). Installation and construction will take four to six weeks, as will start-up and certification. Thus, at least 8 months lead time should be planned.

Depending upon the size of the project and the project budget, conducting a factory acceptance test (FAT) before the system is shipped may be desirable. This requires some member of the project team to visit the vendor and evaluate the performance of the system on the shop floor. An excellent checklist has been developed by EPRI (EPRI, 1993) for conducting such an evaluation.

One of the most common problems noted during factory acceptance tests is that the data acquisition system software is not completed (Porter, 1990). Although the system hardware may be fully functional, an essential subsystem basically will be nonoperable. Caught between contract requirements and regulatory deadlines, this scheduling failure is often overlooked, with the expectation that the DAS will be ready sometime during the on-site installation. Approving the FAT without the data acquisition system will be the beginning of trouble in the CEM program. Nonadherence to contractual conditions at this point can lead to further exceptions and delays during installation.

Installing the system will require the cooperation of plant personnel, the vendor, and either plant or subcontracted construction engineers. Platforms may have to be constructed, ports installed, and electrical cables run to the sampling site. These activities may be handled by the plant or the vendor, although vendors often prefer not to be responsible for these construction activities. Major problems can develop at this stage if the construction engineers are not fully informed about the purposes of

the CEM system and the vendor's installation requirements. A port installed at a 45° angle may not align with one on the other side, the analyzer cabinet door may bump into the scaffolding hand rail when opened, or no support is provided for the sampling line or electrical cables. Adequate communication will prevent such problems from developing.

The installation of the system will be relatively straightforward. Debugging the system will not be straightforward, particularly for newer systems developed for the measurement of HAPs. Unanticipated interferences, electrical stability, and calibration drift problems are common in the initial stages of operation. Since the daily calibration check routines for HAPs monitors may differ from the traditional usage of calibration gases, the routines themselves may have to be fine-tuned. A daily calibration instability of greater than 2.5% of span may be indicative of a site-specific installation problem. The problem must be investigated and resolved. Calibration stability should be achieved before proceeding with system certification or other approval procedures.

6.9 Approving/Certifying the System

Certification and approval methods for non-criteria pollutant monitoring systems are discussed in detail in Chapter 7 of this manual. The traditional "performance specification test" certification procedures incorporate the "relative accuracy test," which compares the continuous monitoring measurements to those obtained using an EPA reference method. Performance specification test procedures have proven to be an excellent means for certifying monitoring systems for criteria pollutants. However, validated methods exist for only about 40 of the 189 air toxics materials listed under Title III of the Clean Air Act and these for only a very limited range of sources. This lack of appropriate test methods limits the application of similar testing procedures for these monitoring systems.

Other approval mechanisms can be considered by the environmental control agency. The Method 301 validation criteria (see Chapter 7) are applicable for short-term test methods, but involve an extensive validation program on a site-specific basis only. Alternative methods have been proposed that incorporate laboratory evaluations with field tests conducted at representative "challenging" applications (Peeler, 1996). Proposed laboratory tests include checks for calibration stability, response time, interference rejection, and linearity. Field tests include techniques such as analyte spiking, direct calibration checks, and sampling system bias tests. Similar methods have been used by Kinner (Kinner, 1996) for FTIR applications in cement kilns.

In other cases, such as for metals (as vapor or as particulate matter combined or uncombined), reference methods may not produce data sufficiently precise to compare to monitoring system data. Calibration standards may not be available or may have to be specially generated. Special spiking procedures may also have to be developed. The limited experience in these techniques with certain materials can transform an intended validation program into a research study. Attention then must be paid to all facets of the validation program. The experimental research design must determine the representativeness of the sample measured as well as the precision and accuracy to which it is measured.

Approval methods also are necessary for parametric monitoring systems (parameter surrogate or predictive). Where validated reference methods are not available alternatives must be considered.

6.10 Implementing the QA/QC Plan and Operating the System

Certification or approval of a monitoring system provides no guarantees that the system will continue generating accurate and precise emissions data. An implemented quality assurance (QA)/quality control (QC) program is necessary if data quality is to be maintained (Jahnke, 1993: EPRI, 1993; Scott, 1995; Carlyle, 1995). A quality assurance plan should be prepared prior to certification and implemented immediately thereafter. Effective programs include standard operating procedures for daily calibration, preventive maintenance, training, and periodic audits. When the quality control functions are being performed routinely, the monitoring system then can be viewed as being operational.

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Chapter 7
Certification and Approval Mechanisms for Non-criteria Pollutant Monitoring Systems; Calibration and Demonstration of Performance

7.1 Introduction

The purpose of this chapter is to aid in understanding how CEM systems are evaluated and approved for use in regulatory applications. Quality assurance procedures that are used on an on-going basis to maintain CEM data quality within acceptable limits are discussed. Understanding these issues is important because, 1) specific technical requirements in this area may constrain the selection of CEM equipment, 2) the complexity of a monitoring program at a particular facility may be significantly affected, and 3) the specification or choice of initial approval procedures and quality assurance activities may affect the cost and risk associated with a monitoring program.

Many non-criteria pollutant monitoring applications present special and difficult challenges in this area. The lack of appropriate calibration materials or procedures, inadequate performance specifications and quality assurance requirements, and the absence of reference test procedures all constrain the availability of non-criteria pollutant monitoring systems. Some of these issues are being addressed by instrument developers and control agencies and progress is being made in resolving problems. Many approaches that have been successful in the field of criteria pollutant monitoring cannot be transferred to monitoring of non-criteria pollutants. An overview of certification and approval mechanisms is presented in Figure 7-1. As indicated on the chart, initial monitor set-up activities are very important considerations for non-criteria pollutant monitors. For such monitors, the type of procedures and approaches used by the equipment supplier or facility personnel to establish proper calibration and operation of a measurement system are quite diverse and are highly dependent on the specific sampling and analysis system under consideration. For some systems, these initial set-up and calibration procedures necessitate understanding the intricacies of the analytical technique, the limitations of calibration check procedures, and the constraints of available calibration standards. The "black box" empirical approach traditionally used for criteria pollutant CEM systems is not applicable to many non-criteria pollutants. For many of these monitors the constraints which affect the initial set-up of the monitor also limit the methods which may be used to demonstrate the performance of the CEM system. Many of the issues associated with the initial set-up and calibration of non-criteria pollutant CEM systems are discussed in Section 7.2.

Methods and procedures used to demonstrate the performance of non-criteria pollutant CEM systems both initially and on an ongoing basis are shown in Figure 7-1. Monitoring system certification is based on determining whether the analyzer is properly calibrated, and if the sampling system can deliver the gaseous compounds to be measured to the analyzer within a prescribed tolerance. A number of ways to assess analyzer calibration and sampling system bias exist. Specifications for non-criteria pollutant monitoring systems generally require a performance specification test that includes calibration drift and accuracy tests. These tests are performed soon after installation of the monitor. Daily calibration checks are performed for virtually all CEM systems to assess data accuracy on a day-to-day basis. For some applications, development of a quality assurance (QA) plan and performing periodic accuracy checks may be required. Existing and proposed regulatory mechanisms for performing the initial certification test, conducting subsequent evaluations of monitor performance, and alternate techniques to assess a CEM system's effectiveness are discussed in Sections 7.3.4, 7.3.5, and 7.4.

Because the existing regulatory mechanisms do not address all of the potential issues and applications for non-criteria pollutant monitors, alternate instrumental protocols and acceptance criteria may be necessary for non-criteria pollutant CEM systems data validation. In some cases, approval mechanisms for instrumental test methods may be modified for this application. Techniques such as dynamic analyte spiking may be necessary to properly evaluate CEM system perfor-

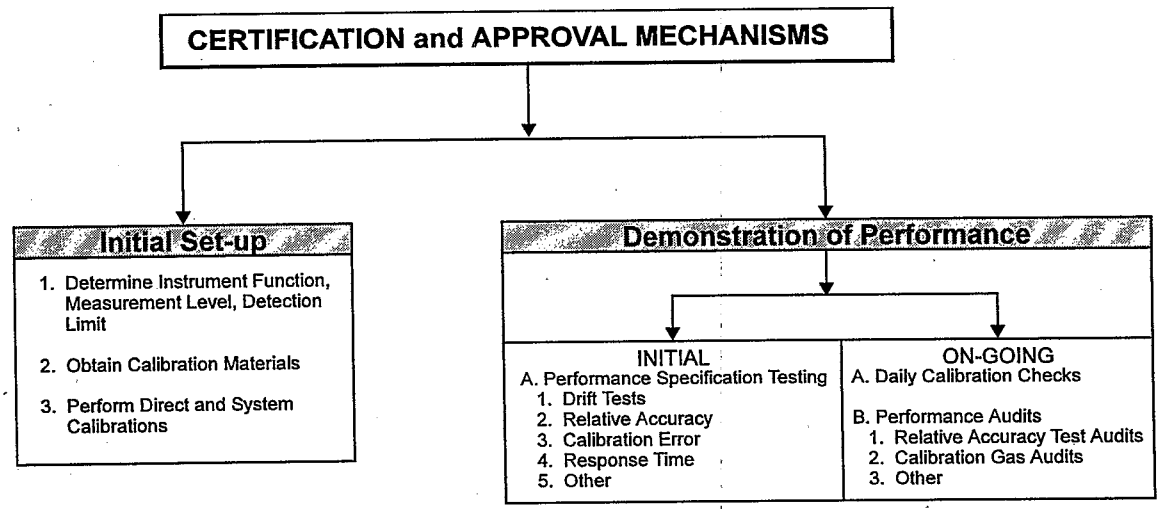

Figure 7-1. Certification and approval mechanisms.

mance necessary to properly evaluate CEM system performance, especially for reactive or condensable compounds, or compounds that have many interferences in the analytical procedures used for quantification. Alternative approaches such as those used in Germany, or those included in standards developed by the International Standards Organization may also be applicable to non-criteria pollutant monitors. These alternative approaches are discussed in Section 7.4.

7.2 Instrument Calibration

The term "calibration" is used to represent many concepts in the CEM field. These concepts include simple daily QA checks, routine adjustments to compensate for analyzer drift, benchtop adjustments made by the manufacturer, comparisons with manual test methods, and fundamental adjustments of various system components. Here, "calibration" is defined as the set of necessary activities that establish the relationship between the analyzer output (instrument response) and a series of standard materials that span the anticipated operating range. In the traditional and most straightforward case, a system measuring gaseous pollutants is calibrated by introducing a series of calibration gases at known concentrations to assess performance. Appropriate adjustments are then made so that the instrument provides a proper response over the measurement range. In other cases, where appropriate calibration materials, performance specifications or quality assurance procedures have not been fully developed, the project manager must evaluate the specific instrument response, the effective measurement range, and the procedures used to establish and verify proper calibration.

In this chapter, the term "analyte" will refer to gaseous compounds that are to be measured. Using this term, calibration can be said to establish the proper measurement system operation for the target analytes.

7.2.1 Instrument Function

"Instrument function" is a term that refers to the instrument's response versus concentration for each analyte. A graphical representation of response versus concentration defines the "shape" of the instrument function. For example, some instruments generate a linear response (i.e., flame ionization detectors, FIDs) through a given calibration range, while other instruments deviate from linearity at low or high concentration ranges (infrared). Some instruments have complex instrument functions such as a logarithmic or quadratic response with respect to concentration.

The instrumental function must be known for each analyte to select the appropriate calibration points over the anticipated operating range. For linear devices such as FIDs, zero and upscale calibration points may be sufficient. However, for non-linear instrument functions, additional calibration points that encompass each analyte concentration are necessary to ensure proper quantification. Figure 7-2 is a simplified representation of two instrument functions.

Multi-component analyzers frequently have different instrumental responses (response factors) for each gas (analyte) that is being measured. In all cases, the instrument function depends upon the analytes' physical properties and interferences from other flue gas components. For example, an FTIR analyzer

may exhibit a linear response for most compounds over a certain measurement range but will exhibit a non-linear response for compounds such as carbon monoxide.

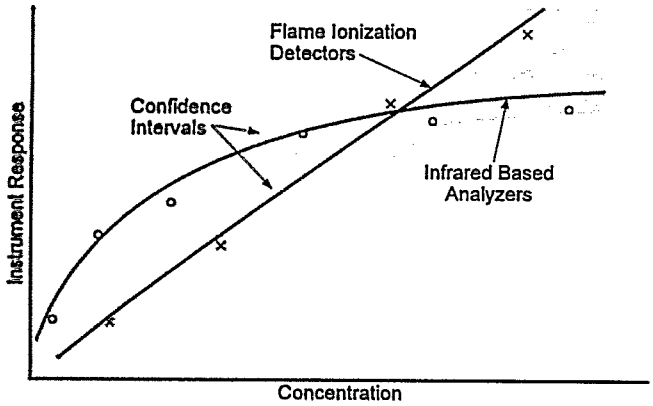

Figure 7-2. Instrument Function of Two Analyzers.

Inherent to the instrument function is the detection level achievable for each analyte. The "detection level," or detection limit, is defined as the lowest concentration level for each analyte that the instrument is able to measure. The detection limit often is determined by the instrument's "signal to noise (S/N) ratio." This is the ratio of the instrument response to the lowest level calibration standard, divided by the instrument response when no analytes are present (noise) which gives a good approximation of the S/N ratio, and thus the instrument's detection limit. An instrument S/N ratio of 10 should be adequate to detect most analytes; however, this should be verified by direct observation.

Another important characteristic of the instrument function is the range of uncertainty associated with the response. Many optical instruments are very repeatable. On the other hand, mass spectrometers exhibit greater imprecision in their quantitative output. Imprecision should not be mistaken for bias. The level of repeatability or precision associated with a specific instrument function must be considered in determining the appropriate number of calibration check repetitions to perform and in establishing control limits for initiating corrective action.

7.2.2 Calibration Materials

Calibration standards may be comprised of certified gaseous standards in gas cylinders, permeation or diffusion devices that generate known concentrations of gas, optical filters, gas filled cells, chemical solutions, or reference spectra. The target analytes, sampling system, and analytical techniques determine which type of calibration standard should be used. Regulatory requirements, the instrument function, CEM system design and the expected target analyte concentration range must be considered when selecting calibration standards. In general, a CEM system calibration technique should provide for checks at a zero, a mid-point, and a high-range concentration for each target analyte.

When certifying and calibrating multi-component analyzers, all, or as many of the analytes as possible, should be in the same gas cylinder or set of permeation/diffusion vials. This will enable simultaneous calibration and calibration checks to be conducted providing for both cost and time savings. The calibration standard manufacturer should be contacted to ensure that calibration standards are available as stable blends at the required concentrations.

7.2.2.1 Gaseous Standards

Virtually all extractive systems can analyze calibration gas directly. Many point in-situ analyzers can analyze calibration gases also. Use of standard reference materials (SRMs) for routine calibrations is cost prohibitive. However, secondary calibration gas standards, called Protocol 1 gases, are referenced to the SRM, and are lower in cost. For some gases, SRMs are available from the National Institute of Standards and Technology. Protocol 1 (USEPA, 1996a) gases are certified by the gas manufacturer under a protocol accepted by EPA. Analyzers that accept calibration gases directly can use Protocol 1 gases (±1-2%), certified reference standards (usually ±2 to 5% accuracy), or permeation and diffusion devices that generate a known concentration of gas. Also, Part 51, Method 205 provides for the dilution of calibration gases for multi-point calibrations to reduce the number of cylinders and amount of gas that is required.

Protocol 1 gases have a period for which they are certified, whereas merely certified reference materials usually do not. Calibration standards for non-criteria pollutants usually are not available as Protocol 1 gases, and therefore, the best available standards are those that have reference values certified by the manufacturer. All calibration standards should be checked periodically to ensure that the compounds have not degraded from their certified values. Suspect calibration gases should be reanalyzed and recertified. Compounds that are particularly problematic in compressed gas form are those that are reactive or have the tendency to polymerize. Examples of these gases are halogenated acids (i.e., HCl and HF) and formaldehyde, respectively.

Some compounds are not available in gaseous form because their vapor pressures are too low, or they are not stable at elevated pressure. Gas standards for these compounds can be generated from the liquid or solid material using either permeation tubes (for liquids) or diffusion vials (for solids). Permeation tubes are sealed devices that contain the analyte and usually are constructed from semipermeable Teflon™ tubing. Diffusion vials are constructed from glass or quartz and have a small orifice through which they are filled with the solid material. Gas generators and permeation/diffusion apparatus are available with emission rates certified within ±2 to 5 percent.

The generation of gaseous standards from liquids or solids is fairly simple. A sample of the liquid or solid contained in the vial is placed in a temperature controlled oven through which a carrier gas is swept. The concentration of the generated gas is directly proportional to the permeation/diffusion rate of the tube or vial. Permeation and diffusion rates are based upon the vapor pressure of the compound, the temperature and pressure of the oven, and the flow rate of the carrier gas. Figure 7-3 is a generalized schematic of a permeation/diffusion based gaseous standards generator.

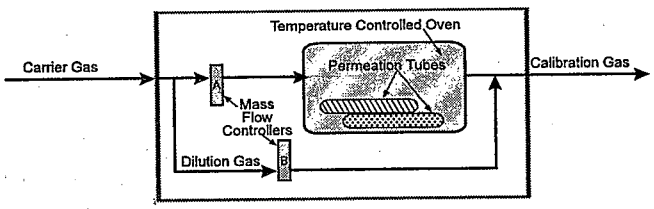

Figure 7-3. Generalized schematic of a permeation/diffusion-based calibration gas generator.

Another means of generating gaseous standards is termed the "hanging drop" approach. In this procedure, a drop of the standard solution is introduced into a gas stream via a syringe. The syringe assembly is placed into a heated compartment so that the drop is continuously volatilized by carrier gas. Use of the hanging drop technique involves many parameters that introduce errors that could invalidate test results. Factors such as preparing the standard solution and determining the exact volatilization rate affect the resultant concentration of analyte in the calibration gas, and thus the accuracy of the calibration. This procedure should be used only when certified gaseous standards and permeation/diffusion standards are not available commercially.

7.2.2.2 Reference Spectra

Some analyzers employ reference spectra standards for calibration purposes. Reference spectra may be used repeatedly without having to recalibrate the analyzer, and thus provide savings in cost and time. Fourier transform infrared (FTIR) and tunable diode laser analyzers are examples where reference spectra standards are used to quantify data. A reference spectrum is composed of digitally stored data obtained from an instrument's spectral response to a known gas standard, acquired at a known concentration, temperature, pressure, and measurement pathlength. These spectra represent graphically the instrument's response (relative absorbance of electromagnetic radiation) with respect to wavelength. To employ reference spectra acquired at one point in time to quantify data acquired at a later date, the instrument response obtained during reference spectral acquisition is compared with the instrument response obtained during the time of data collection. A comparison of the instrument response at different points in time is performed by analyzing a calibration transfer standard (CTS). Similarly, reference spectra acquired on one instrument may be used to quantify data collected on another instrument provided that the two instrument responses are related through the CTS.

The CTS gas is used as the link between the instrument response at the time of calibration and the instrument response at the time of actual sample acquisition. A CTS spectrum generated during instrument calibration is compared to a CTS spectrum acquired during sampling. A mathematical transformation (correction factor) is then applied to match the reference spectrum CTS to that acquired during sampling. The exact same process is used to adjust the reference spectra so that they represent the instrumental response at the time of sampling, and therefore may be used to quantify data.

Figure 7-4 is a simplified diagram of the use of calibration transfer standards. In this figure, the CTS gas collected during field sampling is 0.85 times the response of the CTS collected with the reference spectra. Therefore, to employ the reference spectra, a mathematical transformation must be applied to the CTS reference spectrum to match the CTS collected with the sample spectrum, and thus adjust for the difference in instrument response. This same transformation is then applied to the analyte reference spectrum to quantify the analyte in the sample spectrum.

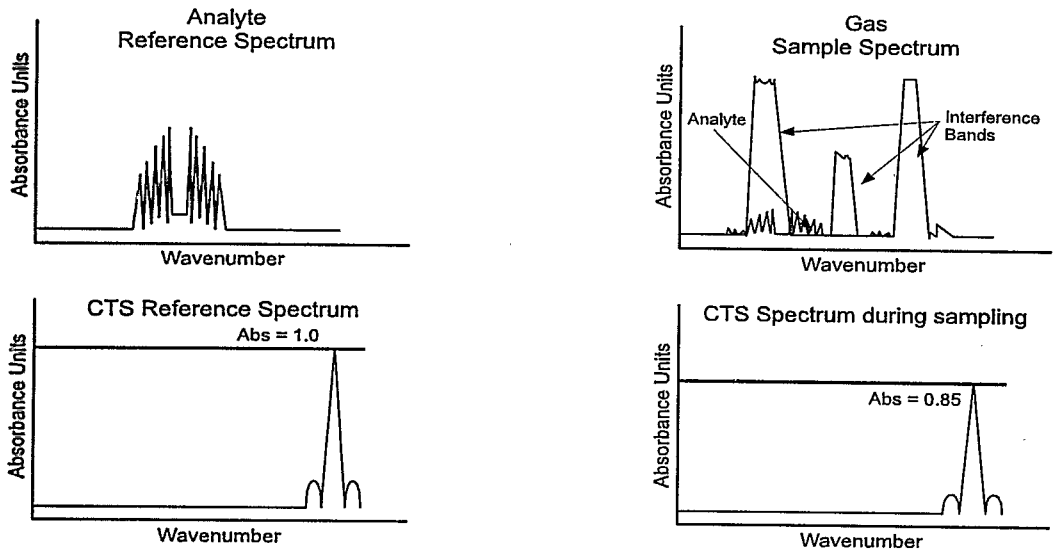

Figure 7-4. Use of calibration transfer standards (CTS).

The concept of calibration transfer is simple in theory; however, in practice it may be quite complex. In theory, any set of reference spectra may be used provided that the calibration transfer is valid. In practice, reference spectra are most often generated on the actual field instrument to minimize errors associated with the necessary CTS mathematical transformations and added noise. Detailed procedures for acquisition of FTIR reference spectra standards and their transference are beyond the scope of this text. These may be found in an EPA FTIR Protocol (USEPA, 1996b).

7.2.2.3 Other Calibration Techniques

Some analyzers are not capable of directly accepting calibration gases. Many cross-stack in-situ analyzers are not designed to accept calibration gases while the design of others allows the use of a flow-through gas cell. The approach used to check the calibration for these monitors also may be constrained because the flue gas cannot be removed from the measurement path and thus the zero concentration is difficult to verify. Some in-situ monitors have been designed or modified to allow the introduction of calibration gases (Jahnke, 1993, 1994). For many of these instruments, the calibration gas cell must be maintained at the same temperature as the flue gas sample to obtain valid calibration measurements.

For in-situ gas analyzers that cannot analyze calibration gases, a zero reflector or other device may be used to simulate the zero concentration condition. Calibration standards may be comprised of a gas-filled cell or an optical filter that is inserted into the measurement path to generate an upscale instrumental response. Where gas cells are mounted within a temperature controlled region of an analyzer, temperature compensation features that are used in the sampling mode may need to be disabled to adjust for optical absorption and/or gas density variations in the flue gas. In this situation, calibration checks with gas cells may not represent fully the performance of the entire measurement system. Problems in the temperature compensation feature cannot be detected if it is disabled during the calibration checks. When a significant component of the monitoring equipment is excluded from the routine calibration check procedure, a separate means of verifying the performance of the excluded component must be used.

The primary calibration for most in-situ analyzers that cannot accept calibration gases is established typically during laboratory bench tests at the manufacturing facility. Based on the design of the instrument, various internal functions are monitored to maintain performance within acceptable limits or to provide an indication to the operator that the initial calibration is no longer valid. The parameters and functions that are monitored depend on the analytical principal and the design of the instrument. Understanding the relationship among these parameters and the acceptable tolerances is usually more complex than simply evaluating a monitor response to an external calibration standard.

Some analyzers employ a correlation factor derived from comparing the instrumental response to another sampling method. The initial instrument function is determined, and the initial calibration is conducted by setting and monitoring internal instrumental parameters. Then the instrument response is correlated to concentration by comparison with reference test methods. Polynuclear aromatic hydrocarbon (PAH) analyzers are an example of such instruments. Calibration is factory set, and correlation to concentration is performed by comparing the instrument response with EPA Office of Solid Waste Method SW846-0010/8270 (SW846 Manual, Nov-ember 1986). This instrumental correlation to reference method determined concentration must be performed on a source-by-source basis.

Continuous particulate monitors are another example of analyzers calibrated by correlation to manual sampling methods. This can be accomplished in accordance with the provisions of the International Standards Organization 10155 (ISO, 1995, see also 7.3.4 CEM System Approval Mechanisms in Germany, or the proposed Part 60, Performance Specification 11A). This standard establishes performance specifications and procedures for performing the calibration of continuous particulate matter measurement techniques relative to the results of a series of manual tests. Recalibration is required when conditions change at the facility that may affect the calibration.

For particulate monitors, the specific parameters that are monitored on a day-to-day basis (or in some cases on a continuous basis) depend on the measurement technique. For example, transmissometers used as particulate monitors incorporate a simulated zero mechanism (often a reflector to simulate zero opacity) and an internal optical filter (as an upscale check) to verify proper performance. Similarly, in-situ light scattering devices used as particulate monitors include a two point calibration check by temporarily not illuminating the effluent and by using the light source and a filter to check the response of the detector. These and other internal checks are sufficient to determine that the instrument operates within the limits established by the manufacturer.

7.2.3 Direct and System Calibration Procedures

Once the instrument function and necessary calibration materials are determined, the monitor may be calibrated. There are two conventional calibration methods for CEM systems that accept calibration gases. These methods are referred to as "direct" and "system" calibrations, respectively. Figure 7-5 is a generalized schematic of direct and system calibrations.

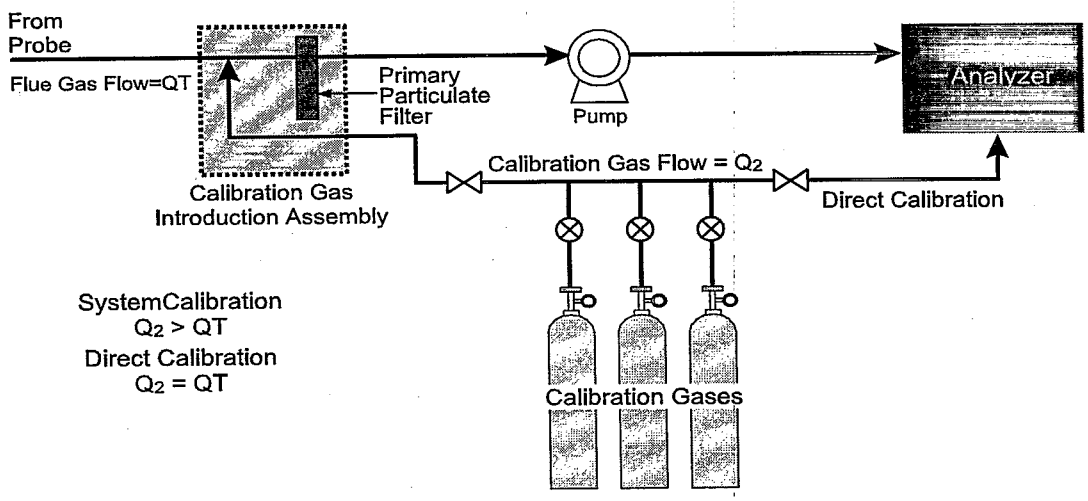

Figure 7-5. Direct and system calibrations.

A direct calibration consists of injecting the standards directly at the analyzer and recording the response. Direct calibration checks assess the stability of the analyzer and the extent to which the instrument has drifted from its zero and span calibration points. Direct instrument calibrations test the instrument function only.

A system calibration injects the calibration standards at a point in the sample delivery system as close to the probe tip as possible. Calibration standards must be introduced at a point upstream of the primary particulate matter filter to account for any filter/particulate cake reactions with the analytes. System calibrations provide an indication of the sample handling system's effectiveness to deliver the analytes to the analyzer, as well as testing the instrument function.

Optimally, direct and system calibrations should agree. Large differences between these two calibration techniques for the same analytes could indicate that a leak is present or that losses due to chemical or physical reactivity are occurring. Losses due to adsorption and condensation are the most typical for non-criteria pollutants. System calibrations are also necessary to determine if compounds may have adsorbed on the filter. Adsorbed or condensed compounds that volatilize later can cause a positive measurement bias.

For those analyzers that measure multiple components, daily calibrations of the instrument may not be economically feasible for all compounds that are measurable. In this instance, surrogate compounds must be chosen for calibration checks. Surrogates are target analytes that can also represent a range of other target analytes through similar instrumental response, sampling system bias response, and other important characteristics. Selection of surrogates depends on their ability to represent more than one of the target analytes, based on similar physical properties. An example of surrogate selection is the use of one water soluble compound to represent many. If a CEM system is designed to measure HCl, formaldehyde, acetaldehyde, ammonia, methanol, and benzene, toluene and xylenes (BTX), the use of HCl and benzene may be possible as surrogates for the entire population of compounds. HCl will represent the water soluble and reactive compounds, while the benzene can represent the aromatic compounds. Protocols using surrogate recovery check compounds have been prepared by the Portland Cement Association based upon using surrogate compounds (Kinner, 1995). In these protocols, three recovery check compounds were used to represent fourteen volatile organic compounds to reduce the cost and complexity of the testing program.

Optical analyzers that employ a reference spectral library for quantification also need to perform calibration status checks on a periodic basis. This ensures that a valid calibration transfer exists between the time of reference spectra acquisition (reference library) and the time of sample collection and analysis. A gaseous calibration transfer standard (CTS) should be analyzed and the response compared to the response at the time the reference spectra were obtained. Direct and system calibrations using the CTS should be performed so that the effect of sampling system bias on instrumental response may be measured. Ethylene and carbon monoxide have been successfully used as calibration transfer standards for extractive FTIR measurement systems (USEPA, 1993; Kinner, 1994).

Software audits also can be used as a tool to evaluate optical CEM system quantitative algorithms and their ability to accurately quantify data. Software audits may consist of synthetic spectra (a number of reference spectra superimposed upon one another), or actual measurement data that challenges the ability of the analysis technique to distinguish between the target analytes and their interferences. Such audits can be useful where a computer is used to analyze broad-band spectral measurements such as those employed by an FTIR. In such cases, the selection of particular spectral regions over which to perform an analysis, or the particular procedure used to remove the affects of water or other interferences, may significantly affect the results.

An audit using artificially generated spectra, or spectral data files from prior measurements obtained at another source, can be employed to gauge the effectiveness of the analytical procedure. However, audits are likely to generate one-sided conclusions. For example, an analysis routine that cannot properly identify target analytes in an audit spectrum most likely will fail to identify these analytes in actual samples. The converse is not necessarily true. Obviously, a software audit cannot evaluate the physical performance of a sampling system or the performance of an analyzer.

7.3 Demonstration of Performance; Certification and Quality Assurance

CEM systems installed to comply with regulatory requirements must demonstrate acceptable performance both initially and on a continuing basis. The

specific requirements vary for different regulatory applications (see Chapter 2) or according to specific conditions or requirements included in the facility's permit. Nevertheless, most CEM systems are subject to a performance specification test, or "certification test," soon after installation. Source operators are required to perform daily checks of CEM systems calibration status to ensure the validity of data on a day-to-day basis. Some sources are required to develop quality assurance plans and conduct periodic audits of CEM systems performance. In other cases, the regulatory agency relies on a general requirement for the proper operation and maintenance of the CEM system and can require performance specification tests to be conducted as necessary.

7.3.1 EPA Performance Specifications for Non-criteria Pollutant Monitoring

Performance specifications are a set of procedures and criteria that are used to evaluate the acceptability of the CEM system at the time of installation and whenever specified in the applicable regulations. Existing EPA performance specifications (PS) for non-criteria pollutant analyzers address monitoring of VOCs and TRS only. Performance specifications for H_2S in refinery fuel gas also have been developed to provide an alternative to measurement of SO_2 emissions at many emission points. Existing EPA performance specifications for non-criteria pollutants are summarized in Table 7-1 (requirements from PS 2 are shown for comparison).

Performance specifications for VOC CEM systems are included in PS 8 and PS 9 of Part 60 for sources subject to New Source Performance Standards. PS 8 is applicable to analyzers that provide a total hydrocarbon response and PS 9 applies to analyzers that speciate hydrocarbons using a gas chromatograph. Neither of these performance specifications require the use of a specific type of detector.

Performance specifications for hydrocarbon monitors also are included in 40 CFR, Part 266, Appendix IX for sources regulated by the boilers and industrial furnaces (BIF) rule, and in 40 CFR, Part 503 (subpart E) for sewage sludge incinerators. These specifications require a heated sampling system and heated flame ionization detector (FID) analyzer.

Performance specifications 8A for hydrocarbons, 10A for multi-metals, 11A for particulate matter (PM), 12A for mercury (Hg), 13A for hydrochloric acid (HCl), and 14A for chlorine (Cl_2) monitors are proposed in the hazardous waste combustor rule. (FR 4/19/96) This proposed rule covers both hazardous waste incinerators and BIF sources. These performance specifications will be included in Part 60 if this proposed rule is adopted. All of the performance-based specifications listed above are derived from PS 2, ISO 10155 (for particulate monitoring), and various instrumental test methods.

7.3.2 Performance Specification Testing

A performance specification test (PST) is performed soon after installation of the CEM system and periodically as specified in the applicable regulations. The test is performed in accordance with procedures detailed in the applicable performance specifications previously described. In some regulatory applications (and in common usage), this initial test is referred to as a "certification test." The PST usually includes a calibration drift test and an accuracy test. (For Part 75 applications, the term "calibration error test" is used to describe the drift test and daily zero and upscale calibration checks. This terminology is avoided here to minimize confusion.) The accuracy test is often a "relative accuracy test" involving comparison with results of an independent reference test method (RM). For some monitors, the accuracy test requires analysis of several calibration standards to determine calibration error only. Depending on the specific regulatory requirements, the PST also may include response time or cycle time tests, short-term drift tests, and demonstrations that the measurement system can operate continuously for prescribed periods without unscheduled maintenance or repairs. (Part 75 performance specifications are described in Chapter 2, Acid Rain Program.)

7.3.2.1 Calibration Drift Test

A typical PST includes a calibration drift test performed over 7 consecutive days. The calibration drift test evaluates the stability of the monitor response to the procedure used for daily checks of the monitoring system (see also Daily Calibration Checks). The calibration drift test is conducted by introducing the zero and span gases, gas cells, optical filters, or electric signals to the system and recording the instrument response. The deviation of the instrument response at the zero and upscale calibration point must meet the applicable criteria. For example, the allowable calibration drift in PS 8A is 2.5% of the span. Therefore, a hazardous waste incinerator required to monitor hydrocarbons subject to PS 8A has an allowable analyzer span value of 100 ppm, and may have a maximum of ± 2.5 ppm drift at the zero and span level for each 24-hour period over the seven consecutive days during the performance specification test. The tester is allowed to adjust the calibration accordingly after each daily check during the drift test.

Table 7-1. Existing Performance Specifications for Selected Pollutant Monitors

PS #	40 CFR	PERFORMANCE SPECIFICATION TEST				DAILY CALIBRATION REQUIREMENTS
		Calibration Drift	Calibration Error	Relative Accuracy	Response Time	
2* SO_2 NO_x	Part 60 Appendix A	7 day test 2.5% of span	N/A	±20% of Reference Method or 10% of standard	N/A	zero and span drift within 2X's PST before required adjustment
5 TRS	Part 60 Appendix A	7 day test 5% of span (6/7 days)	N/A	Same as PS2	N/A	Same as PS2
7 H_2S in fuel gas	Part 60 Appendix A	7 day test 5% of span (6/7 days)	N/A	Same as PS2	N/A	Same as PS2
8 Total VOCs	Part 60 Appendix A	Same as PS2	N/A	Same as PS2	N/A	Same as PS2
9 GC CEMS VOCs	Part 60 Appendix A	N/A	7 day test 3 injections at three levels Precision and Linearity $r^2 = 0.995$ CE ≤10% for all levels	Performance Audit during CE testing ±10% criteria	<5 minutes or as specified	Triplicate mid-level calibration checks must be within 10% of certified value or repeat initial 3-point calibration
BIF[1] THC	Part 266 Appendix IX	7 day test 3% of span Annual PST	5% of span for all calibration points	N/A	120 seconds for 95% step change	zero and span drift <3 ppm
SS**[1] THC	Part 503 Subpart E	7 day test zero and span within 6%	zero within 5 ppm mid- and span within 10 ppm	N/A	200 seconds for 90% step change	Same as PS2

* Included for comparison purposes
** Sewage Sludge Incinerators
1 No number assigned

7.3.2.2 Relative Accuracy Test

Relative accuracy (RA) tests are required for almost all criteria pollutant CEM systems except for opacity monitors. A relative accuracy test is also required for certain non-criteria CEM systems. The RA may be conducted concurrently with the 7 day calibration drift test. The relative accuracy test involves comparing the average CEM system response with the integrated average pollutant concentration or emission rate for each corresponding reference method test run. A minimum of nine RA comparative test runs are required; however, EPA specifications allow the rejection of up to three test runs. Therefore, 12 runs usually are performed in practice with the best nine results used in the RA calculations. The RA specification for a CEM system subject to PS 8 is ≤20% of the average reference method (RM) result or ≤10% of the applicable emission standard, whichever is greater.

Relative accuracy calculations are based upon the results of at least nine comparative runs. The difference between the run averaged CEM system results and the reference method is calculated and averaged. The absolute value of the summed differences for each run plus a confidence coefficient (CC) is divided by the average of the reference method values (RM_{ave}):

$$RA = [|d| + CC]/RM_{ave} * 100 \quad \text{Equation 7-1}$$

The confidence coefficient is expressed in terms of a statistical t-value according to the following equation for a t-value at a = 0.025 for n-1 degrees of freedom:

$$CC = t_{0.975}(S_d/n^{1/2}) \quad \text{Equation 7-2}$$

Where

$t_{0.975}$ = Corresponds to the probability that a measured value will be biased 2.5% at the 95% confidence level.

S_d = The standard deviation of the differences of the 9 data pairs.

n = Number of test runs.

As shown above, the relative accuracy result includes both mean difference and confidence coefficient terms based on the paired CEM system and reference test results. Both the accuracy and precision of the paired measurements are evaluated. A user must recognize that the relative accuracy is affected by the accuracy and precision of both the monitoring system and the reference test method. Failure of a relative accuracy test may be due to problems with the CEM system, problems with the reference test methods, problems with the representativeness of the sampling location, or other factors. A failed test requires careful investigation to determine the cause, after which the test must be repeated.

Relative accuracy is based on comparing concurrent monitoring data and reference method test results. Therefore, the response time of the CEM system must be taken into account to directly compare the monitoring with the reference method results. Where instrumental reference test methods are used, the response time and sampling frequency of the reference method must be considered also. For relative accuracy tests with these systems, sampling runs must be of sufficient duration to allow comparisons of valid averages obtained from both the CEM system and the reference system.

Where CEM systems are compared to reference methods that provide integrated results (e.g., impinger trains and most other manual methods), the exact start time and stop time for manual sampling runs (and time associated with interruptions for port changes or other problems) must be included. When substantial changes in emission concentrations or emission rates occur over the course of the run, or when short duration spikes occur during runs, comparisons between integrated reference methods and CEM systems are often invalid.

The relative accuracy comparison of a CEM system to a reference method assumes that the RM generates accurate and precise data, and that the source testers have adequate experience in correctly executing the reference method. Interferences affecting the test method results can be mistaken for bias in the CEM system measurements. Use of an imprecise test method increases the magnitude of the confidence coefficient in the relative accuracy calculation. Similarly, the imprecision due to sloppy or inexperienced testers can affect the results dramatically. These issues were initially of great concern in criteria pollutant monitoring applications but eventually were minimized through experience and development of more precise instrumental test methods for use in place of wet-chemistry methods for most applications. For non-criteria pollutant monitoring applications, these factors are still of great concern because: 1) interferences affect some reference methods when extended to new applications, 2) sample recovery documentation and other QA criteria are not included in all methods, 3) lower and potentially variable emission concentrations are encountered, 4) the precision of some methods is

poor and for some other methods is unknown, 5) some methods are not demonstrated fully where they applied before promulgation of standards at the specific source category, and 6) source testers have much less experience in using these methods for performing relative accuracy tests. In summary, an imprecise, inaccurate, or improperly conducted reference method test will increase the probability that the CEM system will fail the PST even if it is functioning and calibrated properly.

Further disagreements may result in relative accuracy testing due to actual technical limitations. For example, PS 8 includes a relative accuracy specification, however, the only reference method that generates a total hydrocarbon response is EPA Method 25A (Part 60, Appendix A), which specifies the use of a flame ionization detector (FID). Method 25A is the only reference method directly comparable to a CEM system installed to satisfy PS 8. However, PS 8 does not specify the use of a particular detector; it simply specifies instrumentation that generates a total hydrocarbon response.

Presuming that the CEM system uses an FID, then the relative accuracy test would involve comparing two FID measurement systems. Because the two systems use the same analytical technique, interferences within the effluent stream could go undetected. Additionally, differences in the compound-specific response factors between two FIDs could affect the outcome of the relative accuracy test even though both systems are properly calibrated using the same standard (Cone, 1989).

Also, consider the example where a photoionization detector (PID) is chosen for the CEM system installed to comply with PS 8. A relative accuracy comparison with a Method 25A FID may not be appropriate because PID and FID responses differ substantially for different classes and functional groups of hydrocarbons. Because neither the CEM system nor the reference method provides any information regarding the speciation of individual compounds within the flue gas, one is unable to decide whether apparent agreement or disagreement between the CEM system and the reference method was due to differences in response factors or other calibration/accuracy issues. In this case, the outcome of the relative accuracy test is likely to be indeterminate and may generate more controversy than answers.

The BIF and sewage sludge incinerator performance specifications for hydrocarbon monitors, and the proposed PS 8A, specify using a heated FID and heated sampling system. PS 8A requires a three-point calibration error test rather than a relative accuracy test comparison using Method 25A. This approach avoids the relative accuracy test issues described above for PS 8. However, the three-point calibration error test, using calibration gases, provides only a limited evaluation of the monitoring system. (See also Section 7.3.2.3.)

Proposed performance specifications 10A (multi-metals CEM systems) and 12A (mercury CEM systems) include relative accuracy specifications (USEPA, 1996c). Although multi-metals CEM systems are not commercially available at this time, prototypes have been developed using a variety of approaches. Limited field tests have been conducted. Calibration standards and techniques, measurement sensitivity, and accuracy are critical technical issues for these developing measurement systems. The accuracy and precision of proposed Method 29 has not been demonstrated to allow for relative accuracy testing of multi-metals CEM systems over the expected range of pollutant concentrations (Brown 1996, Laudal 1996). Modifications to proposed Method 29 are being developed.

Mercury may exist as elemental mercury (Hg^0) and as other oxidized Hg (Hg^+, Hg^{+2}) species in effluent streams. Mercury CEM systems generally sense elemental mercury and employ sample conditioning elements that convert all mercury in the sample stream to this form (Richards, 1996, Roberson, 1996). (See also Chapter 3.) Proposed EPA Method 29 attempts to speciate the different oxidation states of mercury. Studies have been conducted on coal-fired facilities to evaluate the performance of Method 29 by spiking elemental mercury and $HgCl_2$ (Laudal, 1996). These investigators have shown that the presence of significant quantities of SO_2 (>1,500 ppm) and the presence of 10 ppm chlorine (Cl_2) affects substantially the collection of elemental mercury and the determination of mercury species present. Other mercury test methods have been shown to be affected significantly by the presence of NO_x in the sample stream. Until the performance of the manual test methods are understood and the effluent conditions that affect the results are well known, an appropriate and reliable relative accuracy test procedure cannot be devised for mercury CEM systems.

Proposed PS 13A and PS 14A for HCl and Cl_2 specify calibration gas audits instead of comparison to reference methods. The reference method for HCl and Cl_2 is EPA Method 26A, which collects the gaseous components in an impinger train and

measures the dissociated chloride ions by ion chromatography. Proposed PS 13A and 14A specify that HCl and Cl_2 must be measured in the gas phase as opposed to the measurement of the dissociated chloride ion in solution. A cylinder gas audit only is required in these performance specifications, not a relative accuracy test employing Reference Method 26. HCl continuous emission monitoring requirements in Pennsylvania; however, require a relative accuracy test using Method 26. Pennsylvania requirements do not mandate that HCl and Cl_2 be measured in the gas phase.

Even where reference methods have been developed for the pollutants of interest, the comparison of CEM system and RM data may not assess the ability of the CEM systems to measure the compounds of interest accurately. Consider for example measurement of formaldehyde which is a very water soluble, reactive compound and which may polymerize in sample delivery systems. Several reference methods exist for the collection and measurement of formaldehyde. These methods rely on sample collection in high purity water, the Parosanaline Method (EPA TTN EMTIC BBS, 919-541-5742); in dinitro-phenyl hydrazine (DNPH) impregnated silica gel tubes, NIOSH Method 3500, (NIOSH 1994); or in sampling trains containing DNPH (SW846-0011). The results provided by all three of these methods are biased by the presence of other aldehydes and ketones (Serne, 1993). In addition, the reaction of formaldehyde with DNPH is very pH specific. The two DNPH methods are sensitive to the presence of acid gases (e.g., HCl, SO_2, H_2SO_4, etc.) and base gases (NH_3). Thus, the use of these methods at any source having significant concentrations of these compounds in the flue gas would affect adversely relative accuracy test results for a formaldehyde CEM system.

In summary, relative accuracy specifications and test procedures have long served as the primary evaluation standard for the acceptability of criteria pollutant CEM systems. For some non-criteria pollutants and monitoring applications, the relative accuracy test continues to play an important role in demonstrating performance and certifying CEM systems. However, for other applications relative accuracy tests are inappropriate or must await future development of appropriate reference test procedures.

7.3.2.3 Calibration Error Tests

As used here, a "calibration error test" consists of multi-point comparison of monitor response to a series of calibration materials. (The usage of "calibration error test" varies. In the Part 75 Acid Rain Program, this term is used to refer to calibration drift tests and daily checks. In Part 75, the term "linearity test" is used to refer to multi-point accuracy tests relative to calibration materials.) In certain applications, as indicated below, the calibration error test is required in place of the relative accuracy test. However, in other regulatory applications, both a calibration error test and a relative accuracy test are included in performance specification tests.

As previously mentioned, BIF and sewage sludge incinerator performance specifications for total hydrocarbon monitors, and proposed PS 8A, do not include a relative accuracy test but instead require a calibration error test to determine the accuracy of the monitoring system. The test involves analysis of a zero gas and two upscale calibration gases. The calibration gases used for these tests are propane in a balance gas of nitrogen. The instrument response of these measurement systems to different compounds (i.e., "response factors") is known to vary as a function of: 1) the number of the carbon atoms, 2) the degree of carbon bond saturation (carbon double and triple bonds) within the molecule, 3) the presence of chlorine, and 4) other instrument-specific factors. However, the determination of these response factors is not included in the calibration error test. Furthermore, the effect of other effluent stream constituents (e.g., moisture, CO_2, CO, O_2, NO_x, etc.) on the accuracy of the monitoring data can not be determined by the calibration error test. The calibration error test in this case may therefore not adequately validate the monitoring system for actual flue gas hydrocarbon measurements.

PS 9 applies to CEM systems that employ a GC to separate organic compounds. As with PS 8, it also does not specify a particular type of detector. Multiple target analytes are speciated by an instrument-specific calibration curve generated from certified calibration standards. A preliminary calibration error test of the analyzer is accomplished by analyzing low-level (40-60%), mid-level (90-110%), and high-level (140-160%) calibration standards that represent the percent of the measured concentration levels for all analytes. A screening test using the appropriate instrumental test method may be required to identify the effluent analytes and determine their relative concentrations.

The PST required by PS 9 includes a performance audit test and a seven-day calibration error (CE) test period during which the initial instrument perfor-

mance is evaluated. The CE is performed daily by analyzing calibration standards at each level in triplicate (3 analyses X 3 levels = 9 analyses/day). The calibration error for each analyte is determined by comparing the average instrument response for each level of triplicate analyses to the certified reference value of the calibration standards. The calibration error may not exceed ±10% for each analyte.

The performance audit test required by PS 9 consists of analyzing an EPA audit gas during the seven-day CE test. This test is intended to provide a somewhat independent check because the audit gas must be obtained from a different supplier than the gases used for the CE test. The concentration of the analytes in the audit gas generally are not known to the user.

7.3.2.4 Response Time Tests and Cycle Time

The measurement system response time is important for monitoring applications with short averaging or reporting periods or where spikes in the effluent concentration occur. The sampling system response time is determined by monitoring the instrumental response to a calibration standard while performing a system calibration. Upscale and downscale response times are determined by introducing high-range and zero calibration gases respectively. System response time is defined as the time it takes the analyzer to reach 95% of the step-change in concentration.

Determination of the measurement system response time can be important even when it is not specified in the applicable regulations. The system response time must be considered when conducting the relative accuracy test. For measurement systems that accept calibration gases, the system response time must be known so that calibration gases are introduced for a sufficient period to provide a stable measurement response.

Some regulations specify the frequency for obtaining measurements. 40 CFR 60.13 specifies that all measurement systems must complete a cycle of sampling, analysis, and data recording at least once during each 15 minute period. In contrast, BIF regulations specify that a sample must be acquired and analyzed every 15 seconds. The average emission rate is computed and recorded at least every 60 seconds, with an hourly rolling average calculated each minute. Usually, the cycle time is immediately apparent from the design of the CEM system and programming of the data acquisition and handling equipment. In some cases, time-shared extractive systems are used to allow a single set of analyzers to monitor emissions from several locations. Other functions such as particulate filter or sampling line blow-back or purges may also be included for certain CEM systems. These functions must be considered when determining the cycle time for some systems.

7.3.2.5 Other Performance Test Criteria

Some regulations include additional performance specifications and test procedures. For example, transmissometers may be used as particulate mass concentration monitors and as opacity monitors. These instruments, if subject to the proposed revisions to Performance Specification 1, would be subject to a short-term drift test to detect diurnal variations in monitor performance. This drift test includes zero and upscale calibration drift checks at one-hour intervals over a period of 24 hours. Similar short-term drift tests were included in Part 60 performance specifications prior to 1983 and are included in some state monitoring requirements (e.g., Pennsylvania).

Many performance specification test requirements include an "operational test period" during which the CEM system must operate continuously without unscheduled maintenance or repairs. This is typically a one week (168-hour) test. Such a test period may seem insignificant for a measurement system that is intended for continuous monitoring over a period of many years. However, early experience with criteria pollutant monitoring systems revealed that this was a difficult specification for many CEM systems to meet. Although much progress has been made in improving the ruggedness and reliability of conventional systems, the application of new technologies or new measurement systems attempting to utilize laboratory instruments may require that more attention be devoted to achieving reliable operation.

7.3.3 Ongoing Performance Checks and Quality Assurance

Additional performance checks and quality assurance activities are required to be performed after initial installation, calibration, and performance testing (certification) of a CEM system. In general these include whatever is necessary to properly operate and maintain the monitoring system, daily calibration checks to determine the ongoing validity of the data and, in some cases, periodic quality assurance audits.

7.3.3.1 Daily Calibration Checks

Daily calibration checks are the primary basis for evaluating the validity of data on a day-to-day basis. This is of fundamental importance for many sources because 1) reporting of emissions data is based on daily averages, 2) monitor availability may be expressed as a percentage of valid source operating days, and 3) monitor control limits and the corresponding requirement to initiate corrective action are based on the daily calibration check responses. Also, enforcement of regulations under the Clean Air Act is based on the specific days during which a source is considered to be in violation of applicable regulations. Thus, the daily calibration checks for CEM systems provide the critical determination of validity for each day that data are recorded.

As discussed in Chapter 2, the General Provisions of the Part 60 new source performance standards include requirements to conduct daily zero and calibration drift checks for all CEM systems. Specifically, 60.13 states,

> "(d) (1) Owners and operators of all continuous emission monitoring systems installed in accordance with the provisions of this part shall check the zero (or low-level value between 0 and 20 percent of span value) and span (50 to 100 percent of span value) calibration drifts at least once daily in accordance with a written procedure. The zero and span shall be adjusted whenever the 24-hour zero drift or 24-hour span drift exceeds two times the limits of the applicable performance specifications in Appendix B. The system must allow the amount of excess zero and span drift measured at 24-hour interval checks to be recorded and quantified, whenever specified. ..."

Similar requirements are found in the general provisions for Part 61 and Part 63 NESHAP requirements. Most state regulations also contain similar provisions.

For monitors that accept calibration gases, the daily calibration checks usually are performed by conducting system calibrations using zero and mid- or high-range calibration gases. Using an upscale calibration value that approximates either the pollutant concentrations or the level corresponding to the emission standard is preferred. Most, but not all, regulations require that the calibration gases for extractive systems are introduced at or "as near as practical" to the probe outlet so that as much as possible of the sampling system is checked. Some regulations specify that only gases meeting EPA Protocol 1 (USEPA, 1996a) be used for daily calibrations. Other regulations do not specify a traceability protocol or other standard for calibration gases. Such approaches emphasize the use of the daily checks as a stability test and rely on initial and periodic accuracy tests to ensure that monitoring data are accurate.

For in-situ analyzers, daily calibration checks typically include zero checks and upscale checks using the appropriate signals, filters, cells, or other calibration jig assemblies. The approaches that are used are quite diverse depending on the type of instrument to be calibrated. The approaches used for conducting daily calibration checks may rest on a number of important assumptions or conditions which may not be known or well understood by the user. In practice, these assumptions may become invalid because conditions change that result in daily calibration procedures that do not provide results which are representative of monitor performance. Therefore, a thorough understanding of the daily calibration check procedure and its limitations is important to interpret results correctly.

Additionally, many of the approaches that have been used in the past for daily checks of in-situ analyzers do not evaluate important functional parts of the monitoring instrumentation. As previously described, temperature compensation circuitry is often disabled when checking in-situ monitors using calibration gas cells within the analyzer. In this case, errors arising within the temperature compensation circuitry (which can significantly bias the CEM system measurement results) are likely to go undetected. A thorough understanding of the daily calibration check procedure is needed to interpret results correctly.

An important aspect of the §60.13 (d)(1) regulation is that it requires a written procedure to be developed and followed for performing the daily calibration checks. (For certain sources, this procedure is included in the quality assurance plan.) This written procedure should take into account the important details regarding the calibration of the specific monitor. For extractive systems, it should indicate where the gases are introduced, how the values of check gases are established, provisions to ensure that the gases are injected at the proper flow rate

and pressure, etc. For in-situ monitors, the procedure should specify exactly what is done and it should contain the important assumptions or other conditions that must be maintained for operation of the instrument. Alternatively, the procedure should prescribe the appropriate actions to take when unacceptable performance is observed.

Most importantly, the written procedure provides a standard operating practice to be followed during the initial performance test and each day that emissions data are recorded. In this way, initial and periodic accuracy tests serve to verify the adequacy of the calibration procedure. Implementing the daily calibration procedure verifies the data each day until the next accuracy test is performed. The daily calibration check procedure must conform with applicable regulatory requirements and must also accommodate the technical and practical constraints of the sampling and analysis system as described previously in Section 7.2.

For both extractive and in-situ CEM systems, daily calibration checks are performed and adjustments to the CEM system are required if the indicated drift exceeds specified control limits. When such adjustments are made, or when other corrective action is undertaken, a daily calibration check must be performed after these activities are completed to demonstrate that the monitor has been returned to service properly. Records of adjustments, corrective actions, and the results of daily drift tests are required by virtually all regulatory monitoring requirements.

7.3.3.2 Quality Assurance/Quality Control

40 CFR 60, Appendix F, Procedure 1 contains QA procedures for CEM systems used to demonstrate compliance with emission standards. Although non-criteria pollutant monitoring is not specified as the compliance demonstration method in Part 60 regulations, many permits and state regulations applicable to such monitors adopt Appendix F, Procedure 1 or very similar provisions. The quality assurance procedures for CEM systems in the acid rain program are contained in Part 75, Appendix B and are similar in principal to the Part 60 requirements. Part 75 requirements require that all monitors be able to analyze calibration gases.

Appendix F, Procedure 1 requires that sources develop and implement a QC program with written procedures that describe in detail the complete, step-by-step procedures for calibration of CEM systems, calibration drift determination and adjustment procedures, preventative maintenance, data recording calculations and reporting, accuracy audit procedures, and corrective action procedures for malfunctioning CEM systems. The results of the daily drift determinations are used within Procedure 1 to determine if the CEM system is in control. Procedure 1 specifies that a monitor system is out-of-control if the zero or high-level response exceeds either 1) twice the Appendix B calibration drift performance specification limit for five consecutive days, or 2) four times the Appendix B calibration drift performance specification limit on any one day.

Appendix F, Procedure 1 requires that sources conduct accuracy audits once each calendar quarter. For systems that can use calibration gases, the accuracy audits may include cylinder gas audits conducted during three of four calendar quarters and a relative accuracy test conducted during the other quarter. Alternatively, relative accuracy audits may be performed instead of cylinder gas audits for three quarters. A relative accuracy audit is simply a three-run relative accuracy test evaluating only the mean difference between the CEM system and the RM. The relative accuracy test required by Appendix F, Procedure 1 is identical to the test required during the initial performance specification (i.e., "certification test").

One can see from the above, which is confirmed by experience, that the selection of a CEM system is constrained by the applicable QA requirements. The cost and inconvenience of conducting three cylinder gas audits per year is much less than the cost and inconvenience of conducting three relative accuracy audits per year. The majority of criteria pollutant CEM systems incapable of analyzing calibration gases were excluded from compliance monitoring applications based on this requirement.

7.3.4 CEM System Approval Mechanisms in Germany

Other approval mechanisms have been used internationally that may serve as models or may contain elements that are useful for certification of non-criteria CEM systems. For example, Germany has implemented a rigorous and comprehensive approval process for many years for CEM systems installed for regulatory purposes. Frequently when monitoring equipment used in Europe is first offered for sale in the United States, potential suppliers will claim that the measurement system is "TÜV certified." Various control agencies have indicated interest in these certification procedures and they may be useful in the evaluation of non-criteria pollutant monitors in the absence of EPA approval procedures. The German approach to monitor approval and TÜV

certification often are misunderstood and sometimes misrepresented in the United States. For these reasons, information regarding CEM system QA requirements in Germany are described below.

Monitoring equipment must first successfully complete certification testing by the TÜV before it can be sold for use in regulatory programs. This is a rigorous technical evaluation of each equipment model to ensure that it is suitable for particular applications. In addition, testing and evaluation is performed for each monitor at the time that it is installed and this testing is repeated every three to five years depending on the type and size of the facility. This initial calibration program for monitors in Germany is similar to performance specification tests for monitors in the United States. Additional tests are performed by an independent authority on an annual basis to verify performance of the monitoring equipment. Finally, maintenance procedures are performed by the facility's personnel on an ongoing basis in accordance with the manufacturer's instructions and results from the suitability test.

7.3.4.1 Initial TÜV Certification (Suitability) Tests

Each instrument model must first pass a Technischer Überwachungs-Verein (TÜV) certification before it may be offered for sale in regulatory monitoring applications. The TÜV certification is a rigorous evaluation requiring at least three to six months to complete and includes both laboratory evaluations and field suitability testing. The fee for a TÜV certification test is substantial (typically $50,000 to $100,000) and is paid for by the monitor manufacturer. Repeating portions or all of the certification test increases the cost to the manufacturer. Basic TÜV monitor performance specifications are listed in the Table 7-2. The reproducibility specification demands that two randomly selected instruments provide readings with a mean difference of less than 3.3% over a three-month period. The reproducibility specification also ensures that instruments of the same model number are interchangeable. Zero and calibration drift are limited to ±2% over the maintenance interval. The instrument must provide an alarm indicating the need for immediate maintenance when zero or calibration drift limits are reached. The time needed to reach these limits defines the maintenance interval. The maintenance interval is recommended by the manufacturer but is determined by the TÜV as part of the suitability tests. The maintenance interval should be at least one week; however, four weeks is preferable. Determination of the maintenance interval based on suitability tests and drift limits (relative to the maintenance interval) provides incentives for manufacturers to build stable instruments.

Tests to determine the effects of line voltage variations, ambient temperature variations, and other factors that may influence monitor performance are also performed as part of the TÜV certification. The TÜV may investigate other areas or issues that are considered to be relevant to the performance of a particular measurement system. Field suitability tests are performed for each type of application (e.g., gas-, oil-, coal-, refuse-fired boilers) but in some cases, success at more difficult monitoring applications is taken as a sufficient demonstration for less demanding applications.

7.3.4.2 Initial and Periodic Monitor Calibration Tests

These tests are in many ways similar to CEM system performance specification tests performed in the

Table 7-2. Principal Performance Specifications for TÜV Suitability Tests of Emission Monitoring Instruments

System Parameter	Criteria
Analytical Function (ma vs. concentration)	By Reference Method (regression analysis)
Detection Limit	2% of most sensitive range
Reproducibility	R = measurement range ≥ 30 mean difference
Zero and Calibration Drift	± 2% in maintenance interval
Availability	90% in three months minimum; 95% is the goal
Interference from other species	± 4% of full scale
Maintenance interval	Determined by test program (limited to three months maximum)

United States. However, a number of important differences exist in both the philosophy, nomenclature, and procedures used for these tests. The term "calibration" as used in VDI 3950, Part 1, "Calibration of Automatic Emission Measuring Instruments" refers to the entire process of establishing and verifying the correct performance of a monitoring system (VDI 3950). This includes: 1) procedures for the selection and preparation of measurement sites, 2) procedures to check for proper installation of equipment, 3) leak checks of extractive monitoring systems, 4) a five-point verification of the instrument characteristic (similar to calibration error in the United States using zero and upscale calibration gases), 5) monitor-specific procedures for evaluating measurement interferences, 6) zero and reference (upscale calibration) drift stability tests, 7) response time tests, 8) procedures for measuring and processing data, 9) procedures for checking the representativeness of sampling points, 10) procedures for determining the analytical function for the complete measuring system relative to independent flue gas measurements (reference methods), and 11) procedures for analysis and reporting of the calibration results.

In the United States, many of the calibration issues that are specifically addressed by VDI 3950, Part 1 are either lumped together and evaluated as a group during the relative accuracy test or are simply ignored. For example, the German procedures evaluate separately: 1) the representativeness of the sampling points, 2) the influence of interferences, and 3) the system performance relative to independent emission measurements through a series of tests. In the United States, we rely on a single relative accuracy test to determine the acceptability of all of these factors taken together. The German "calibration" procedure also relates test procedures and results back to the initial TÜV certification test. For example, the calibration interference test procedures specifically address the measurement interferences identified during the initial certification because this is obviously dependent on the specific monitor design and analytical principal. Also, the zero and reference point drift determinations are determined relative to the maintenance interval established during the initial certification test rather than an arbitrary time interval.

The German comparison with independent reference methods relies on a minimum of fifteen paired measurements (CEM and reference method) conducted at different emission levels to facilitate a regression analysis that is used to determine subsequent emission levels. Linear or quadratic regression analysis may be used and calculations of the confidence coefficient and tolerance intervals are included. These statistical quantities also are employed in the interpretation of the monitoring data.

The field calibration test is performed by an independent expert agency (the TÜV) authorized by the German government to perform these evaluations. However, the TÜV office that performs the calibration test at a particular industrial facility is not necessarily the TÜV office that performed the initial certification. Again, the field calibration procedure is performed initially and then is repeated every three to five years depending on the type and size of the facility.

7.3.4.3 Annual Calibration Tests and Maintenance
Section 8, "Periodical Functional Test" of VDI 3950, Part 1 describes the annual evaluation requirements. These include: 1) checks of the operational status (leak checks, optical contamination, etc.), 2) records review of zero and reference point checks, 3) zero and reference drift tests, 4) checks for interferences, 5) multi-point verification of the instrument characteristic (calibration error test) using zero and upscale calibration gases or other calibration materials, 6) certain monitor functional tests, 7) a minimum 4-run comparison with independent reference methods, and 8) inspection of the data transmission to the chart recorder, integration device, or data logging system. These are more extensive evaluation procedures than are required for monitors subject to EPA regulations. These procedures also are performed by an independent licensed agency (TÜV) rather than by source personnel. Maintenance is performed by the industrial facility's trained personnel. Minimum procedures are specified for in-situ devices and for extractive systems.

7.3.5 International Standards Organization
International Standards Organization (ISO) has developed standards for certain monitoring applications. ISO Standard 7935 is for SO_2 CEM systems and the standard for NO_x CEM systems is currently in draft form (ISO, 1991). A discussion of these standards for criteria pollutant monitoring and a comparison with United States regulations is presented by Jahnke (Jahnke, 1993). Other ISO standards for emissions test methods are under development.

The ISO committee TC146/SC1/WG1 has prepared ISO standard 10155 "Stationary Source Emissions, Automated Monitoring of Mass Concentration of Particles - Performance Characteristics, Test Procedures, and Specification". The standard, prepared over the last 10 years, was published in its final form on April 1, 1995 (ISO, 1995). It does not prescribe a particular method or analytical technique but instead reflects a general approach and provides performance

specifications to evaluate any specific method that is offered. Fundamental to the ISO standard is the requirement to perform a site-specific calibration or correlation to ISO manual method 9096 (which is similar to EPA isokinetic particulate sampling methods) (ISO, 1991). As should be expected, ISO 10155 specifies that the calibration procedure must be repeated when changes in emission controls, fuel type, or other factors occur that may be expected to influence the calibration. Although this is a general requirement, it reflects the fact that the need for recalibration is best based on practical judgment.

ISO 10155 prescribes several performance specifications including the following:

- Response time of less than 1/10 of the manual sampling time
- Zero and span drift less than ±2% of working range per month
- Accumulated automatic zero and span adjustments less than 6% of working range
- Calibration (correlation) line specification
  1. Correlation coefficient ≥0.95
  2. 95% confidence interval shall be ≤10% of emission standard
  3. Tolerance interval; 95% confidence that all possible values are within ±25% of emission standard

The ISO 10155 standard requires that sample runs be performed at three different emission levels to establish the calibration. A minimum of 9 sampling runs must be performed but 12 or more runs typically are expected. The ISO standard prescribes that the process operating conditions should be varied if possible to create the different emission levels. Where this is not possible, variation of the control equipment operating parameters to create a range of emission levels is accepted.

The Central European Normalization Committee (CEN committee TC264/WG5) is developing requirements applicable to continuous particulate monitoring (Peeler, 1996, b). Unlike ISO, which is a voluntary organization of participating countries, CEN mandates requirements for the 14 countries comprising the European Community. The CEN committee will establish: 1) emission standards and limits, 2) manual test methods, and 3) automated monitoring methods. Each participating country must adhere to the CEN requirements or adopt more restrictive/more rigorous requirements. CEN typically adopts ISO standards/methods where available. The CEN committee has adopted the ISO 10155 continuous particulate monitoring standard and applied it as a requirement for hazardous waste incinerators.

The calibration line specifications are illustrated in Figure 7-6.

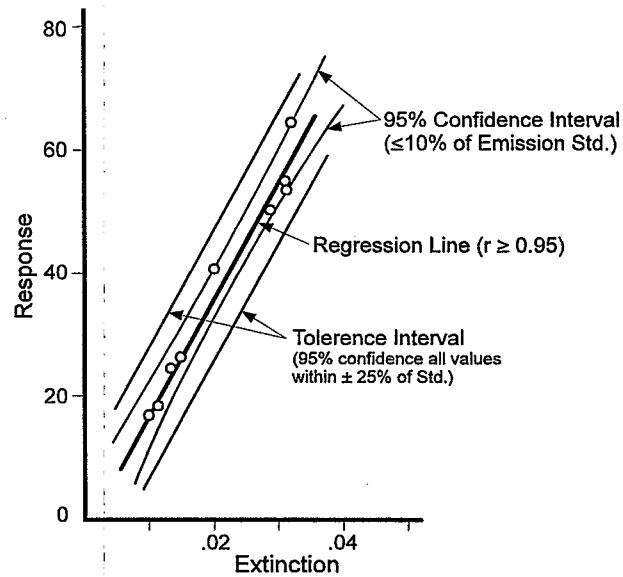

Figure 7-6. Continuous particulate monitoring calibration line specifications.

7.4 Suggested Approval Mechanisms and Approaches for Non-criteria Pollutant and Application Testing

The requirements and procedures discussed in Sections 7.3.1-7.3.3 for conducting initial performance specification tests and audits are consistent with existing regulatory programs and can be used for many non-criteria pollutant monitoring applications. However, some of these procedures do not address problems fully that may be encountered in evaluating non-criteria CEM systems. New evaluation procedures likely will be needed as technology continues to evolve and as monitoring applications for additional specific non-criteria pollutants expand through regulations, permit requirements, or market based trading programs. Several alternative approval mechanisms that may be applicable in these situations are described in this section.

7.4.1 EPA Method 301

Method 301 of Part 63 (USEPA, 1996a) is an approval process designed for industrial sources to use in the development of alternate test methods in the absence of other validated methods, or in cases where an alternate method is desirable. Method 301

initially was developed to allow a specific source to demonstrate the validity of a hazardous air pollutant test method for that source to qualify for an "early reduction" option. Method 301 was intended to encourage development of methods where methods did not already exist. The practical application of Method 301 has been expanded greatly beyond its original purpose; it now serves as a model for evaluating many measurement methods for both criteria and non-criteria air pollutants.

Method 301 incorporates procedures to determine if the precision and bias of a candidate method are acceptable based on comparisons with a validated method, use of isotopic spiking, or analyte spiking. Method 301 is directed primarily at traditional source testing approaches that include discrete sampling and analysis phases. The implementation of the procedure requires the use of quad-trains or paired sampling trains to evaluate precision and bias. Alternative procedures have been developed and accepted by the EPA to allow the application of Method 301 to direct interface methods (methods where the effluent is directly injected into the analyzer) such as instrumental methods using FTIR and GCMS analytical techniques (USEPA, 1994). These alternative Method 301 procedures include collecting a series of spiked and unspiked effluent data for calculation of the precision and bias of a method. These analyte spiking procedures have been used to demonstrate the acceptability of various test methods used by industry in MACT standard development programs (Kinner, 1996, LaCoss, 1995).

Note: Method 301 is only a source specific test method determination. Method 301, Section 12 includes a general discussion regarding "conditional approval" of a method which might allow the transfer of results to additional sources. Conditional approval waiver requirements include: method documentation, ruggedness tests, sample stability, and practical limits of quantification. EPA has granted test method approval to groups of sources in several circumstances. A voluntary administrative procedure documenting the applicant's and EPA responsibilities for instrumental field test methods has been proposed by an instrument vendor, and is being evaluated for a direct interface gas chromatograph mass spectrometer method (Peeler, 1996).

As noted above, Method 301 can be adapted to evaluate direct interface or other instrumental test methods. Such methods are similar to CEM systems in that successive samples are acquired and analyzed. However, instrumental test methods generally involve a much more detailed protocol and many more specific procedures than are associated with a CEM system. Also, an instrumental test method usually requires the full time attendance of an operator as compared to a CEM system, which is designed to function automatically with very little human intervention. Because of these differences, many modifications to Method 301 are necessary to apply it to the evaluation of CEM systems.

7.4.2 Dynamic Analyte Spiking

Dynamic analyte spiking involves the quantitative introduction of a calibration gas of known concentration containing one or more analytes, to an effluent sample stream. The spike gas represents only a small fraction of the combined stream. Therefore, the spiked sample stream contains essentially the same constituents at the same concentrations as the unspiked samples. A comparison of spiked and unspiked samples provides an evaluation of both the effectiveness of the sampling system and the performance of an analytical system.

Because of the similarity of the spiked and unspiked samples, "matrix effects" (interference effects due to the presence of other sample constituents such as moisture, oxygen, carbon dioxide, etc.) can be assessed by this procedure. The analyte spiking approach is particularly useful in the evaluation of non-criteria pollutants that are reactive, condensable, water soluble, or that have the tendency to polymerize in the sampling system. These types of compounds represent the most difficult measurement challenges and can invalidate traditional approaches for assessing monitor performance.

Selection of the spike analytes depends upon two items: the number of target analytes, and the ability to obtain these compounds in gaseous form. For multi-component CEM systems, analyte spiking with all of the target analytes may not be economically feasible. In this case, some surrogates that represent the analytes must be chosen. Selection of surrogates depends on their ability to represent more than one of the target analytes based on similar physical properties.

Dynamic analyte spiking is a more rigorous evaluation procedure than the traditional system calibration. Simply introducing dry calibration standards in a system calibration is useful to check for leaks, adsorption/desorption in the sampling system and to check the analyzer calibration. However, even the straightforward absorption of analytes by condensate formed from sample moisture cannot be detected in the system calibration because dry calibration gases are used. Similarly, the system calibration cannot detect

analytical interferences due to analyte interaction with other components present in the effluent samples because the calibration gas does not usually contain these components.

By performing dynamic analyte spiking, the effectiveness of the sample delivery system and the analytical components are assessed more thoroughly for the compounds of interest in the presence of actual source matrix interferences and moisture. This procedure should be performed in conjunction with both direct and system calibrations. Together these procedures provide a check of the CEM system both on a dry basis and under actual sampling conditions.

7.4.2.1 Analyte Spike Procedure

Any CEM system that has the capability to accept calibration gases at a point upstream of the particulate filter is a candidate for analyte spiking. The spike gas is delivered into the sampling system, typically in a ratio of 1 part spike to 9 parts sample gas, resulting in a ten-fold dilution of the spike gas. The spike should not exceed this 1:10 ratio to avoid excessive dilution of the analytes of interest or substantially changing the sample matrix. Figure 7-7 is a generalized schematic of the analyte spiking technique.

The spike gas should be preheated to prevent localized condensation at the point of injection. The spike must be delivered to the sampling system at a point upstream of the particulate matter filter to detect possible gas reactions with the accumulated particulate material on the filter.

Calibrated mass flow meters or controllers are necessary to deliver the spike at a precise, measured flow rate. A calibrated rotometer for measurement of total flow is also necessary. The rotometer should be installed in the sample delivery system at a point that provides an accurate measurement of total sample flow. Experimental errors associated with calculating the dilution factor of the analyte spike arise from the inaccuracy of the spike and total sample flow measurement devices (see Appendix G, Equation G-2). In addition, calibration of the total flow measurement device with wet stack gas can be difficult or impractical. In addition, the effects of errors associated with the analyte spike calibration standard values are also magnified.

As an alternative to the above, the measurement of the spike dilution factor may be determined directly through measurements of a tracer compound contained in the analyte spike gas. A tracer must be chemically inert and not present in the source effluent. Sulfur hexafluoride (SF_6) has been used successfully as a tracer in extractive FTIR test methods, and is included in draft Methods 318 and 320. (Method 318 may be proposed as an FTIR test method for inclusion in 40 CFR Part 63.) The amount of spike gas introduced during a spiking experiment can be determined from the concentrations of the analyte and tracer components of the calibration standard. (See Appendix G). Errors associated with use of the tracer technique are associated with the analyzer's ability to measure the tracer gas concentration accurately and errors associated with the analyte and tracer concentrations in the spike gas standard.

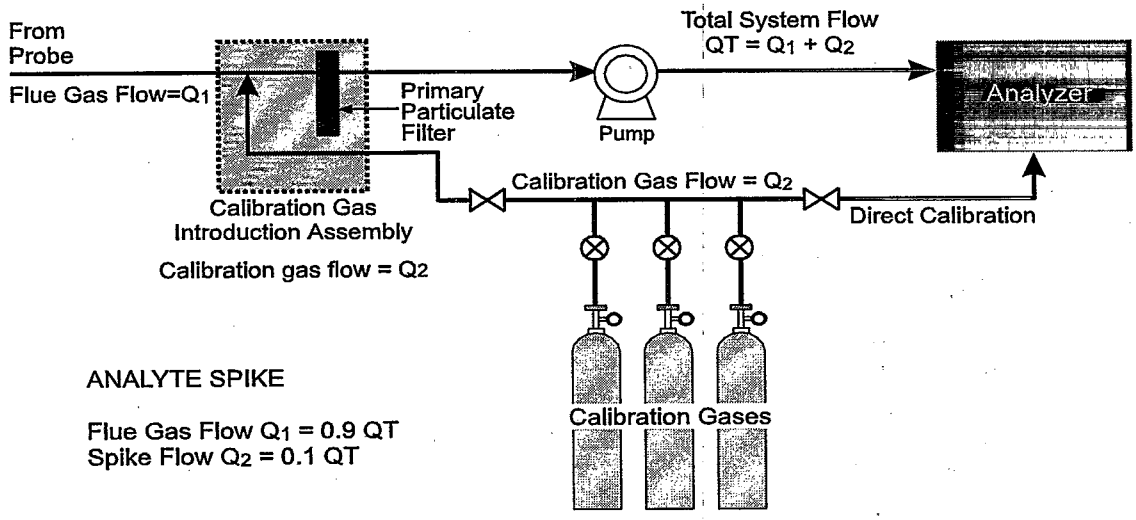

Figure 7-7. Analyte spiking.

Appendices

Appendix A
Acronyms

A&WMA	Air & Waste Management Association
BACT	Best Available Control Technology
BBS	Bulletin Board System
BIF	Boiler and Industrial Furnace
BTU	British Thermal Unit
BTX	Benzene, Toluene, Xylenes
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAM	Compliance Assurance Monitoring
CC	Confidence Coefficient
CEM	Continuous Emission Monitoring
CFR	Code of Federal Regulations
CTS	Calibration Transfer Standard
DAHS	Data Acquisition and Handling System
DAR	Data Assessment Report
DCPL	Demonstrated Compliance Parameter Limit
DCS	Distributive Control System
DEQ	Department of Environmental Quality
DER	Discrete Emission Reductions
DNPH	Dinitro phenol hydrazine
DOAS	Differential Optical Absorption Spectroscopy
DOS	Disk Operating System
DRE	Destruction and Removal Efficiencies
ECD	Electron Capture Detector
EMC	Emission Measurement Center
EMTIC	Emission Measured Technology Information Center
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ERC	Emission Reduction Credit
FID	Flame Ionization Detector
FR	Federal Register
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
HAP	Hazardous Air Pollutant
HON	Hazardous Organic NESHAP
I/O	Input/Output
IR	Infrared
ISO	International Standards Organization
LAN	Local Area Network

LTD	Long Tons Per Day
MACT	Maximum Achievable Control Technology
MARAMA	Mid-Atlantic Regional Air Management Association
NDIR	Nondispersive infrared
NDUV	Nondispersive ultraviolet
NESCAUM	North East States Consortium for Air Use Management
NESHAP	National Emission Standards for Hazardous Air Pollutants
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NSPS	New Source Performance Standards
OAQPS	Office of Air Quality Planning and Standards
O&M	Operation and Maintenance
OMT	Open Market Trading
OMTG	Open Market Trading Guidance
OMTR	Open Market Trading Rule
PEEK	Polyether ether ketone
PEM	Predictive Emission Monitoring
PID	Photoionization Detector
PLC	Programmable Logic Controller
PS	Performance Specification
PST	Performance Specification Test
QA	Quality Assurance
QC	Quality Control
RA	Relative Accuracy
RATA	Relative Accuracy Test Audit
R&D	Research and Development
RCRA	Resource Conservation and Recovery Act
RECLAIM	Regional Clean Air Incentives Market
RTD	Resistance Temperature Device
RTU	Remote Terminal Unit
SCAQMD	South Coast Air Quality Management District
S/N	Signal to Noise
TC	Technical Committee
TCD	Thermal Conductivity Detector
THC	Total Hydrocarbon
TÜV	Technische Uberwachung Verein
TRS	Total Reduced Sulfur
TTN	Technology Transfer Network
USEPA	United States Environmental Protection Agency
UV	Ultra-violet
VDI	Verein Deutscher Ingenieur
VOC	Volatile Organic Compound
WAN	Wide Area Network
WG	Working Group
WTE	Waste To Energy

Appendix B
Glossary

Accuracy - The closeness of the measurement made by a continuous emission monitoring system, a pollutant concentration monitor or a flow monitor, to the true value of the emissions or volumetric flow. It is expressed as the difference between the measurement and a reference method value, which is assumed to be equivalent to the true value. Variation among these differences represents the variation in accuracy that could be caused by random and/or systematic error.

Analyte - A compound or set of compounds that are to be measured by an analytical method.

Analyze - To conduct a measurement and arrive at a specific result or set of results.

Analyzer - An instrument that is capable of performing the measurement of the compounds of interest and generating an output proportioned to the concentration of the analyte.

Acid Gas - A gas comprised of compounds such as SO_2, HCl, or H_2SO_4 that is corrosive in nature and that can be difficult to sample.

Bias - Systematic error. The result of bias is that measurements will be either consistently low or high, relative to the true value.

Blowback - A procedure conducted periodically by some extractive sampling systems during which compressed air is blown out of the sample probe to remove accumulated particulate matter from the probe tip.

Calibration - The procedure for adjusting the output of a device to bring it to a desired value (within a specified tolerance) for a particular value of input (typically the value of the reference standard).

Calibration check - The procedure of testing a device against a known reference standard.

Calibration Drift - The difference between 1) the response of a gaseous monitor to a calibration gas or standard and the known concentration of the gas or standard, or 2) the response of a flow monitor to a reference signal and the expected value of the reference signal, or 3) the response of a continuous opacity monitoring system to an attenuation filter and the previously determined value of the filter after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

Calibration Gas - A gas of known concentration that is traceable to either a standard reference material gas or a National Institute of Standards and Technology or whose concentration is established by an analytical method, on a manufacturer's certification.

Calibration Gas Cell or a Filter - a device that, when inserted between the transmitter and detector of the analyzer, produces a desired output level on the data recorder.

Chemiluminescence - Loss of energy by a chemically excited molecule that results in emission of electromagnetic radiation at a particular wavelength. The energy of the radiation is indicative of the amount and type of species that luminesce.

Chillers - See condenser systems.

Close-coupled - An extractive CEM system that is installed at the sampling location.

Condensate - The resultant water and water soluble compounds that are removed from a flue gas sample by condenser systems.

Condenser Systems - A system designed to physically remove the moisture from the flue gas sample stream by cooling before introduction into an analyzer.

Condensible Gas - A gas that has chemical and physical properties that allow it to change from a gas to a liquid in sampling systems before analysis.

Continuous Emission Monitoring System - The equipment used to analyze, measure, and provide, on a continuous basis, a record of flue gas emissions.

Corrective Action Codes - Entered by the data acquisitions system operator to describe actions taken to correct CEM fault conditions or emission exceedances.

Data Acquisition and Handling System (DAHS) - A system of hardware and software that is used to collect and store emissions data from gas analzyers and to produce summary reports. For regulatory purposes, the DAHS is considered to be an integral part of the CEM system.

Data Acquisition System - One or more devices used to receive, compute, store, and report CEM system measurement data from single or multiple measurement devices.

Data Assessment Report (DAR) - For a CEM system subject to 40 CFR 60, Appendix F, quality assurance requirements, the DAR is a quarterly report which includes all accuracy audit results, reasons for downtime, and corrective actions.

Data Availability - A statistic used to indicate the percentage of plant operating time for which valid CEM system data are available. Some monitoring regulations or permit conditions have minimum data availability requirements for each quarter of the year.

Data Flags - A code that the data acquisition system associates with each data point to identify whether the data point is valid, invalid, or questionable. Data flags are used to determine which data points are included in emission averages.

Data Logger - A simple digital data recorder that can be used to convert gas analyzer output signals to concentrations and emission rates and to calculate averages. Emission results may be printed real-time or stored in memory for later retrieval by computer.

Data Recorder - A device capable of providing a permanent record of data.

Desulfurization - Removal of sulfurous compounds in stack emissions. Often accomplished at utility boilers by use of lime/limestone scrubbers.

DeNox - Removal of oxides of nitrogen from flue gas using selective catalytic reduction (SCR) or non-selection catalytic reduction (non-SCR).

Detector - The device used to sense an analyte in a monitoring system.

Detection Limit - The lower level of quantification achievable by a particular measurement.

Diffusion - The transport of a liquid or gaseous substance through a solid material.

Diluent Gas - A major gaseous constituent in a gaseous pollutant mixture. For combustion sources, carbon dioxide, nitrogen, and oxygen are the major diluent gases.

Direct Calibration - Introduction of the calibration gas directly to an analyzer without passing it through the sampling system.

Distributed Control System (DCS) - A type of computer system used in plant environments for process control. It relies on a system of independent processors that are linked to a central computer.

Drift - Change in analyzer output, over a period of time, that is unrelated to input or equipment adjustments.

Dual Range System - A pollutant concentration monitor that has two distinct ranges of values over which measurements are made.

Emission Standard - The maximum emission level, in specified units, and averaging period allowed by an environmental regulation.

Extractive System - A monitoring system that withdraws a gas sample from the stack and transports the sample to the analyzer.

Flow Monitor - A stand alone monitor, or a component of the continuous emission monitoring system that generates an output proportional to the volumetric flow of exhaust gas.

Hazardous Air Pollutants (HAPs) - Specific pollutants and groups of pollutants listed in Title III of the 1990 Clean Air Act Amendments. (See Appendix D of this handbook.)

Hydrocarbons - Compounds composed of carbon and hydrogen.

In-situ Monitor - A monitor that senses the gas concentration, particulate concentration, opacity, or velocity in the flue gas and does not extract a sample for analysis.

Interference Rejection - The ability of a CEM system to measure a gaseous species, within specified limits, without responding to other gases or substances present in the flue gas.

Invalid Data - Data that were generated while the measurement device(s) was out-of-control.

Linearity - The degree to which a CEM system exhibits a straight line (first order) response to changes in concentration (or other monitored value), over the range of the system.

Lower Detection Limit - The minimum value that a device can measure.

Mass Flow Meter/Controller - A device that is used to measure precisely known volumes for flow rates of gas.

Measurement Cell - The chamber where a gas sample is subject to analysis.

Opacity - The degree to which a flue gas stream reduces the transmission of visible light or obscures the visibility of an object in the background.

Path Continuous Emission Monitoring System - A continuous emission monitoring system that measures the pollutant concentration along a path greater than 10% of the equivalent diameter of the stack or duct cross section.

Point Continuous Emission Monitoring System - A continuous emission monitoring system that measures the pollutant concentration either at a single point or along a path equal to or less than 10% of the equivalent diameter of the stack or duct cross section.

Parts Per Million (ppm) - One part in one million total parts ($1x10^{-6}$).

Parts Per Billion (ppb) - One part in one billion total parts ($1x10^{-9}$).

Path Length - The distance a light beam travels through the a sample gas before reaching the detector.

PEEK™ - A tubing (poly ether ether ketone) substance manufactured to be inert relative to chemical adsorption.

Permeation - Diffusion of a gaseous substance through a solid material.

Precision - The closeness of a measurement to the actual measured value expressed as the uncertainty associated with repeated measurements of the same sample or of different samples from the same process (e.g., the random error associated with simultaneous measurements of a process made by more than one instrument). A measurement technique is determined to have increasing precision as the variation among the repeated measurements decreases.

Programmable Logic Controller (PLC) - An electronic device that can be used to automatically control sampling and calibration cycles and alarm condition responses in a CEM system.

Reason Codes - Entered by the data acquisition system operator at the time of a CEM malfunction or process upset, they are used to describe the reasons for invalid data or emission limit exceedances.

Reference Spectra - Spectra that have been acquired under specific conditions and stored for later use.

Reference value - The known concentration of a verification standard or calibration gas or the known value of a reference thermometer or output value of a temperature, pressure, current or voltage calibrator.

Relative Accuracy - The absolute mean difference between the gas concentration or emission rate determined by a CEM system and the value determined by an appropriate reference method plus the 2.5 percent error confidence coefficient of a series of tests, divided by the mean of the reference method tests. The relative accuracy provides a measure of the systematic and random errors associated with data from a continuous emission monitoring systems.

Remote Terminal Unit (RTU) - An electronic device that is used to periodically report emissions data to the control agency by telephone modem.

Response Time - The amount of time required for the continuous emission monitoring system to display on the data recorder, 95% of a step change in pollutant concentration. This period includes the time from when the sample is first extracted from the stack (if any extractive system is used) to when the concentration is recorded.

Span Gas - A high range calibration gas.

Span - The algebraic difference between the upper and lower range values of the monitoring system or analyzer.

Standard Reference Material - A reference material distributed and certified by the National Institute of Standards and Technology (NIST).

System Calibration - A calibration procedure that directs gas through the entire sampling system.

Stripchart Recorder - A device for recording data in graphical form on a continuous chart.

Test Method - Any method of sampling and analyzing for a substance or determining the flow rate as specified in the applicable regulations.

VEO (Visible Emission Observation) - A measurement of the opacity of a plume by a trained human observer in accordance with EPA Method 9.

Volatility - The degree to which any compound is a gas at specific temperature and pressure conditions.

Appendix C
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Appendix D
Hazardous Air Pollutants 1990 CAAA Title III Listing

CAS NUMBER	CHEMICAL NAME
75070	Acetaldehyde
60355	Acetamide
75058	Acetonitrile
98862	Acetophenone
53963	2-Acetylaminofluorene
107028	Acrolein
79061	Acrylamide
79107	Acrylic Acid
107131	Acrylonitrile
107051	Alyl Chloride
92671	4-Aminobiphenyl
62533	Aniline
90040	o-Anisidine
1332214	Asbestos
71432	Benzene (including benzene from gasoline)
92875	Benzidine
98077	Benzotrichloride
100447	Benzyl chloride
92524	Biphenyl
117817	Bis(2-ethylhexyl)phthalate(DEHP)
542881	Bis(chloromethyl)ether
75252	Bromoform
106990	1,3-Butadiene
156627	Calcium cyanamide
105602	Caprolactam
133062	Captan

CAS NUMBER	CHEMICAL NAME
63252	Carbaryl
75150	Carbon disulfide
56235	Carbon tetrachloride
463581	Carbonyl sulfide
120809	Catechol
133904	Chloramben
57749	Chlordane
7782505	Chlorine
79118	Chloroacetic acid
532274	2-Chloroacetophenone
108907	Chlorobenzene
510156	Chlorobenzilate
67663	Chloroform
107302	Chloromethyl methyl ether
126998	Chloroprene
1319773	Cresols/Cresylic acid (isomers and mixture)
95487	o-Cresol
108394	m-Cresol
106445	p-Cresol
98828	Cumene
94757	2,4-D, salts and esters
3547044	DDE
334883	Diazomethane
132649	Dibenzofurans
96128	1,2-Dibromo-3-chloropropane
84742	Dibutylphthalate
106467	1,4-Dichlorobenzene(p)
91941	3,3-Dichlorobenzidene
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether
542756	1,3-Dichloropropene

CAS NUMBER	CHEMICAL NAME
62737	Dichlorvos
111422	Diethanolamine
121697	N,N-Diethyl aniline (N,N-Dimethylaniline)
64675	Diethyl sulfate
119904	3,3-Dimethoxybenzidine
60117	Dimethyl aminoazobenzene
119937	3,3'-Dimethoxybenzidine
79447	Dimethyl carbamoyl chloride
68122	Dimethyl formamide
57147	1,1-Dimethyl hydrazine
131113	Dimethyl phthalate
77781	Dimethyl sulfate
534521	4,6-Dinitro-o-cresol, and salts
51285	2,4-Dinitrophenol
121142	2,4-Dinitrotoluene
123911	1,4-Dioxane (1,4-Diethyleneoxide)
122667	1,2-Diphenylhydrazine
106898	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
106887	1,2-Epoxybutane
140885	Ethyl acrylate
100414	Ethyl benzene
51796	Ethyl carbamate (Urethane)
75003	Ethyl chloride (Chloroethane)
106934	Ethylene dibromide (Dibromoethane)
107062	Ethylene dichloride (1,2-Dichloroethane)
107211	Ethylene glycol
151564	Ethylene imine (Aziridine)
75218	Ethylene oxide
96457	Ethylene thiourea
75343	Ethylidene dichloride (1,1-Dichloroethane)

CAS NUMBER	CHEMICAL NAME
50000	Formaldehyde
76448	Heptachlor
118741	Hexachlorobenzene
87683	Hexachlorobutadiene
77474	Hexachlorocyclopentadiene
67721	Hexachloroethane
822060	Hexamethylene-1,6-diisocyanate
680319	Hexamethylphosphoramide
110543	Hexane
302012	Hydrazine
7647010	Hydrochloric acid
7664393	Hydrogen fluoride (Hydrofluoric acid)
123319	Hydroquinone
78591	Isophorone
58899	Lindane (all iosmers)
108316	Maleic anhydride
67561	Methanol
72435	Methoxychlor
74839	Methyl bromide (Bromomethane)
74873	Methyl chloride (Chloromethane)
71556	Methyl chloroform (1,1,1-Trichloroethane)
78933	Methyl ethyl ketone (2-Butanone)
60344	Methyl hydrazine
74884	Methyl iodide (Iodomethane)
108101	Methyl isobutyl ketone (Hexone)
624839	Methyl isocyanate
80626	Methyl methacrylate
1634044	Methyl tert butyl ether
101144	4,4-Methylene bis (2-chloroaniline)
75092	Methylene chloride (Dichloromethane)

CAS NUMBER	CHEMICAL NAME
101688	Methylene diphenyl diisocyanate (MDI)
101779	4,4-Methylenedianiline
91203	Naphthalene
98953	Nitrobenzene
92933	4-Nitrobiphenyl
100027	4-Nitrophenol
79469	2-Nitropropane
684935	N-Nitroso-N-methylurea
62759	N-Nitrosodimethylamine
59892	N-Nitrosomorphloline
56382	Parathion
82688	Pentachloronitrobenzene (Quintobenzene)
87865	Pentachlorophenol
108952	Phenol
106503	p-Phenylenediamine
75445	Phosgene
7803512	Phosphine
7723140	Phosphorus
85449	Phthalic anhydride
1336363	Polychlorinated biphenyls (Aroclors)
1120714	1,3-Propane sultone
57578	beta-Propiolactone
123386	Propionaldehyde
114261	Propoxur (Baygon)
78875	Propylene dichloride (1,2-Dichloropropane)
75569	Propylene oxide
75558	1,2-Propylenimine (2-Methyl aziridine)
91225	Quinoline
106514	Quinone
100425	Styrene

CAS NUMBER	CHEMICAL NAME
96093	Styrene oxide
1746016	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79345	1,1,2,2-Tetrachloroethane
127184	Tetrachloroethylene (Perchloroethylene)
7550450	Titanium tetrachloride
108883	Toluene
95807	2,4-Toluene diamine
584849	2,4-Toluene diisocyanate
95534	o-Toluidine
8001352	Toxaphene (chlorinated camphene)
120821	1,2,4-Trichlorobenzene
79005	1,1,2-Trichloroethane
79016	Trichloroethylene
95954	2,4,5-Trichlorophenol
88062	2,4,6-Trichlorophenol
121448	Triethylamine
1582098	Trifluralin
540841	2,2,4-Trimethylpentane
108054	Vinyl acetate
593602	Vinyl bromide
75014	Vinyl chloride
75354	Vinylidene chloride (1,1-Dichloroethylene)
1330207	Xylenes (isomers and mixture)
95476	o-Xylenes
108383	m-Xylenes
106423	p-Xylenes
0	Antimony Compounds
0	Arsenic Compounds (inorganic including arsine)
0	Beryllium Compounds
0	Cadmium Compounds

CAS NUMBER	CHEMICAL NAME
0	Chromium Compounds
0	Cobalt Compounds
0	Coke Oven Emissions
0	Cyanide Compounds[1]
0	Glycol ethers[2]
0	Lead Compounds
0	Manganese Compounds
0	Mercury Compounds
0	Fine mineral fibers[3]
0	Nickel Compounds
0	Polycylic Organic Matter[4]
0	Radionuclides (including radon)[5]
0	Selenium Compounds

NOTE: For all listings above which contain the word "compounds" and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

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[1] X'CN where X = H' or any other group where a formal disocciation may occur. For example KCN or $CA(CN)_2$

[2] includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol $R\text{-}(OCH_2CH_2)_n\text{-}OR$. Polymers are excluded from the glycol category.

[3] includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

[4] includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C.

[5] a type of atom which spontaneously undergoes radioactive decay.

Appendix E
Units of the Standard

Regulations can impose design constraints on a CEM system through the form in which an emissions standard is expressed. Different types of standards have been used by environmental control agencies for a variety of purposes. In these regulations, emissions have been required to be expressed in the following forms:

A. Concentration when expressed in mg/m^3, corrected to standard conditions (20°C, 101.325 kpa)

B. Wet-basis concentration (ppm, mg/m^3) corrected to dry conditions

C. Concentration (ppm, mg/m^3) corrected to 12% (or other percentage) CO_2

D. Concentration (ppm, mg/m^3) corrected to 6% (or other percentage) O_2

E. Mass emission rate (kg/hr, tons/yr)

F. Mass emission rate (thermal) (ng/Joule)

G. Process weight rate (kg/ton of product produced)

H. Control device efficiency (%)

Calculating emissions in any of these forms implies that specific types of instruments or parameters are to be monitored. A control device efficiency requirement implies that measurements must be made both upstream and downstream from the control device. The basic calculations and their implications follow:

A. Concentration when expressed in mg/m^3 corrected to standard conditions (20°C, 101.325 kpa)

$$\bar{c}_{s_{corr}} = c_s \frac{P_{std} T_s}{P_s T_{std}}$$

This calculation is necessary when reporting particulate, metal, or other concentrations in units of mg/m^3 corrected to standard conditions. It implies that both temperature and pressure measurements be made. Note that by applying this correction only, emissions will be expressed on a wet basis. A wet basis calculation can be used to calculate a pollutant mass rate.

B. Concentration (ppm, mg/m^3) corrected to dry conditions

$$\bar{c}_{sd} = \bar{c}_{sw} (1 - B_{ws})$$

When a concentration standard is to be used alone, without subsequently calculating a pollutant mass rate, results typically are required to be expressed on a dry basis. In this case, the flue gas temperature, pressure, and moisture content must be known. For wet-basis monitoring systems such as in-situ systems, in-stack dilution systems, out-of-stack/non-dry dilution systems, and hot-wet source level extractive systems, the moisture content then must be measured, or in the case of stable processes, often is assumed to have a constant value, based on stack test data. For dry-basis source level extractive systems, pollutant gases are measured on a dry basis and a moisture determination is not necessary.

C. Concentration (ppm, mg/m^3) corrected to 6% (or other percentage) O_2

$$\bar{c}_{s_{6\%O_2}} = \frac{\bar{c}_s (20.9 - 6.0)}{20.9 - \%O_2}$$

The expressions given in A and B do not correct for the effects of dilution air. Dilution air corrections are almost always required so that emission's requirements can be normalized between sources. Since dilution air is usually ambient air, the percent oxygen concentration or percent CO_2 concentration is measured to perform the correction.

D. Concentration (ppm, mg/m^3) corrected to 12% (or other percentage) CO_2

$$\bar{c}_{s12} = \bar{c}_s \frac{12}{\%CO_2}$$

This expression gives the dilution air correction in terms of percent CO_2 and requires the use of a CO_2 monitor.

E. Mass emission rate (kg/hr, tons/yr)

$$pmr = c_{sw} Q_{sw}$$

Mass emission rate standards in units of kg/hr or tons/yr are useful because they give directly the pollutant burden to the atmosphere. Calculating a mass emission rate requires either that a flow monitor be installed or that the volumetric flow rate be calculated in some manner from operational parameters. Since flow is always monitored on a wet basis, concentration also must be be determined on a wet basis. Therefore, in-situ dilution or hot-wet source level extractive systems are appropriate for this type of standard. A cool-dry system can be used if moisture is monitored to correct the data back to wet conditions.

F. Mass emission rate (thermal) (ng/Joule)

$$E = \bar{c}_s F_d \frac{20.9}{20.9 - \%O_2} \qquad E = \bar{c}_s F_c \frac{100}{\%CO_2}$$

$$E = c_{sw} F_w \frac{20.9}{20.9(1 - B_{wa}) - \%O_{2w}}$$

$$E = c_{ws} F_d \frac{20.9}{20.9(1 - B_{ws}) - \%O_{2w}}$$

Electric utilities and industrial boilers combusting carbonaceous fuels usually are required to express emissions in terms of mass per unit heat input. These calculations are performed by using the procedures of EPA Method 19, the F-factor methods, which require the measurement of either oxygen or CO_2 to correct for dilution. A number of monitoring options are available using the F factors. If the F_c factor is used, either a wet or dry system can be used provided that both the pollutant and CO_2 are measured on the same basis. If the F_d factor is used, the pollutant and oxygen concentration measurements must be made on a dry basis. If the pollutant and oxygen are measured on a wet basis, the "wet" F factor can be used if the control system does not employ a wet scrubber.. After wet scrubbers, the moisture content must be measured.

G. Process weight rate (kg/ton of product produced)

$$PWR = \frac{pmr}{p}$$

Process weight rate standards are based upon the amount of product produced from the process industries. The first of these types of standards were established in the NSPS nitric acid and sulfuric acid plant and petroleum refinery requirements. The method requires accounting for the mass of the pollutant emitted and accounting for the amount of product produced that is associated with the emissions. This, in general, requires the measurement of the mass emission rate as in E, above, and a determination of the production rate, p. For some industries, such as certain types of sulfuric acid plants, alternative calculation methods based on process parameter measurements have been developed.

H. Control device efficiency (%)

$$\% \text{ Efficiency} = \frac{\bar{c}_{s(in)_{corr}} - \bar{c}_{s(out)_{corr}}}{\bar{c}_{s(in)_{corr}}} \; 100$$

Removal efficiency is required to be reported in some standards. This requires the use of two CEM systems or one time-shared system measuring or extracting sample gas both upstream and downstream from the control device. If a time-shared system is used, with one bank of analyzers, multi-ranging analyzers may be required because of the difference in concentration between the uncontrolled and controlled flue gas stream. Concentration measurements are corrected for variations in diluent gas concentrations (or expressed as thermal mass emission rates) prior to calculating the control device efficiency.

The monitoring requirements of A-H above are summarized in Table E-1.

TABLE E-1. Monitoring Requirements Based upon Conditions of the Units of the Emissions Standard

Eq.	Gases Monitored		Parameters Monitored
A	Pollutant		P, T
B	Pollutant	H_2O or none	
C	Pollutant	O_2	
D	Pollutant	CO_2	
E	Pollutant	None or H_2O	Flow
F	Pollutant	O_2 or CO_2, possibly H_2O	
G	Pollutant		Flow, Production Rate, Parameters
H	Pollutant (Inlet & Outlet)	O_2 or CO_2 (Inlet & Outlet)	

Symbols:

$\bar{c}_{scorr}$	=	average stack concentration in mg/m^3 corrected to standard conditions
c_s	=	uncorrected concentration
P_{std}	=	standard pressure (101.325 kpa)
T_{std}	=	standard temperature (20°C, 493°K)
T_s	=	stack temperature (°K, °R)
P_s	=	stack pressure (kpa)
$\bar{c}_{sd}$	=	average, dry concentration
$\bar{c}_{sw}$	=	average, wet concentration
B_{ws}	=	moisture fraction
$\bar{c}_{s6\%O2}$	=	average stack concentration corrected to 6% O_2
20.9	=	percentage of O_2 in ambient air
$\bar{c}_{s12}$	=	average stack concentration corrected to 12% CO_2
pmr	=	pollutant mass rate
Q_{sw}	=	wet, flue gas volumetric flow rate
F_d	=	dry F factor
F_c	=	F factor for CO_2
F_w	=	wet F factor
B_{wa}	=	moisture fraction in ambient air
PWR	=	process weight rate (Kg, lbs/tonne, ton product produced, for example)
p	=	production rate (units/ton, tonnes/hr, for example)
$\bar{C}_{s(in)corr}$	=	average concentration, corrected for dilution, in gas entering control device
$\bar{C}_{s(out)corr}$	=	average concentration, corrected for dilution, in gas leaving control device
E	=	thermal mass emission rate (ng/J, lbs/MMBtu)

APPENDIX F Guide for Evaluating CEM System Costs

Table F-1. CEM System Cost Elements Checklist

1. Design/planning of the CEM system program - This element includes the identification of all applicable regulations (e.g., standards, monitoring requirements, location requirements, testing and QA requirements, reporting and recordkeeping requirements) and source-specific constraints (i.e., tentative sampling locations, physical installation constraints, effluent conditions, environmental conditions, personnel constraints, etc.). It may also include some amount of training, formal or otherwise, for the person(s) responsible for the design of the system.

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Familiarization with regulations (read, research...)					
B. Resolution of regulatory questions (calls, letters, meetings, etc.)					
C. Source-specific constraints					
1. Review drawings/plans					
2. Inspect source (inspect similar facility if source not yet built)					
3. Identify physical installation constraints, evaluate existing utilities (electricity, air)					
4. Estimate effluent conditions and parameters (based on stack test report reviews, measurements, and/or engineering judgment, etc.)					
5. Estimate environmental conditions					
6. Evaluate personnel constraints (interview process operators, instrument tech., supervisory personnel, and corporate representatives to determine availability, expertise, previous experience, and opinions/bias)					
7. Summarize results of 1.-6. in written form					
D. Training for person(s) responsible for design/planning of the CEM system					

Table F-1. Continued

2. Selection of CEM system equipment - This element includes deciding between component purchases versus system purchases and deciding about support alternatives (i.e., vendor maintenance agreements, emergency repair services, need for instrument training, availability of spare parts, etc.) It also includes the effort and cost associated with a) investigating monitoring technologies and available equipment options, b) developing equipment specifications, c) identifying and selecting potential vendors, d) developing an RFP and performance guarantees, e) evaluating proposals, and f) negotiating and executing a contract with the successful bidder(s).

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Decide on basic approach (general approach, type of monitoring system, components vs. system purchase, level of vendor support, etc.)					
B. Develop written equipment specifications					
C. Identify potential bidders (call other sources, go to trade shows, read journal articles and trade magazines, call consultants, rely on previous experience)					
D. Develop RFP and performance guarantees (Define the monitoring program in terms of the applicable regulations, source specific constraints, as well as the performance specifications and guarantees that are needed. This must be done in accordance with the purchasing practices of the buyer and may also include legal, insurance, performance bonds, and other terms and conditions)					
E. Compile and send out RFP					
F. Conduct bidders meeting and response to questions raised by the bidders					
G. Bidder presentations (some companies allow or require that all or selected bidders make an on-site presentation of their proposal)					

Table F-1. Continued

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
H. Evaluate proposals and select a winner					
I. Negotiate details of the contract, draft and execute the agreement					
J. Administrative costs associated with implementing the contract					

3. Purchase of Capital Equipment - This element should reflect the actual cost associated with the CEM system and would include all components, calibration materials, and support utilities. Technical and administrative time associated with the purchase activity should also be included.

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Pollutant and diluent analyzers					
B. Monitor remote control units and junction boxes					
C. Sample acquisition, sample conditioning, and sample transport equipment for extractive CEM systems					
D. Sample interface equipment (i.e., air purge blowers, filters, etc.) for in situ CEM systems					
E. Signal cables, communications, alarms, etc.					
F. DAHS computers, software, chart recorders, remote readouts, etc.					
G. Support utilities, electrical power conditioners, isolation transformers, lightening protection, compressed air supply, instrument air, air clean-up systems, etc.					
H. Evaluate proposals and select a winner					

Table F-1. Continued

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
I. Negotiate details of the contract, draft and execute the agreement					
J. Administrative costs associated with implementing the contract					

4. CEM System Installation - This element should include costs for a) stratification tests, if necessary (see text), b) agency approval of the monitoring location, if required, c) installation of sample acquisition/conditioning equipment, sample transport lines, analyzers, monitor control units, calibration gases and related equipment, and data handling/recording equipment, d) installation of sampling ports and utilities as well as ladders, platforms and other access to both the monitoring location and the manual testing location, and e) construction of protective shelters and safety equipment.

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Submit proposed monitor locations to the control agency					
B. Discuss agency response					
C. Conduct stratification test if necessary					
1. Assemble equipment or hire testing firm					
2. Travel to source and return					
3. Perform test and reduce data					
4. Write report and letter to the agency					
5. Determine agency's response					
D. Determine alternate monitoring location, if necessary					
E. Install monitor and manual testing ports					

Table F-1. Continued

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
F. Install necessary support utilities (electricity, compressed air, communications, etc.)					
G. Design and erect protective shelters for monitor components and/or manual sampling					
H. Design and install necessary scaffolding and access (i.e., ladders, elevators etc.) for both monitor and manual sampling locations					
I. Receive and check out monitoring equipment from vendor(s)					
J. Supervise and inspect vendor, or install sample probes, sample acquisition equipment, sample lines, analyzers, monitor control units, calibration gases/manifolds, and DAHS					

5. Start-up and Performance Testing - This element should include the costs for start-up and debugging of the system, on-site training, preliminary testing, arrangements for the performance specification test (PST) (e.g., selecting a contractor, pretest meeting, development and submission of a protocol to the agency, safety requirements, etc.) and the actual PST cost including preparation of a test report.

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Observe start-up					
B. On-site training					
C. Debugging and problem resolution during first few weeks					
D. Select contractor for RA test or entire performance specification test					

Table F-1. Continued

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
E. Travel and attend pretest meeting with testing contractor and agency, if necessary					
F. Develop and submit test protocol to agency, if necessary					
G. Notify agency of test dates					
H. Travel and contractor travel for PST					
I. Preliminary testing as necessary					
J. Conduct RA test (source and contractor expenses)					
K. Source personnel conduct drift test and forward data to contractor (assumption)					
L. Contractor prepares report, source reviews report, and submits to agency (assumption)					
M. Allowance to represent likelihood of test postponement					
N. Allowance to represent likelihood of PST failure and subsequent repeat tests					

6. Operation and Maintenance - At a minimum, this element should include the costs associated with performing the manufacturer's recommended maintenance activities. It should also include the costs associated with expected use of spare parts, maintenance of a parts inventory, emergency repair service, etc. Furthermore, this element would include the cost of performing daily zero and upscale calibration checks of the CEM system (including the costs of calibration gases or materials).

Table F-1. Continued

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Spare parts inventory (capital cost plus interest)					
B. Administrative effort to maintain parts and supply inventory					
C. Effort to perform manufacturer's recommended maintenance activities					
D. Daily calibration checks (time to review calibration data and adjust the CEM system if necessary; calibration gas costs)					
E. Corrective action and emergency repair service, if not included in QA costs					

7. Quality Assurance - The costs for this element depend on the applicable requirements. For this example, we assume that requirements similar to 40 CFR 60, Appendix F, Procedure 1 would apply. To estimate these costs accurately, some frequency of failure to meet QA criteria must be assumed. It may be appropriate to estimate costs for participation in, or observation of, agency inspections or audits of the monitoring program.

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Development of QA/QC Plan					
B. Annual and/or quarterly accuracy audits					
C. Daily precision checks					
D. Corrective action for malfunctioning monitors					
E. Agency Inspections or Audits					

Table F-1. Continued

8. Recordkeeping and Reporting Costs - This element should include the costs associated with the preparation of the required periodic reports describing both emissions problems and monitoring problems/events and data quality reports. It should also include the costs associated with maintenance of the records necessary to generate these reports and other records which are required to be maintained on-site for agency inspection. Most companies will have to maintain additional records in accordance with their own internal procedures to substantiate labor and capital expenditures as well as contracts with other involved parties.

ACTIVITY	LABOR HOURS (PM, TECH. MGT, ADM)	LABOR COST	SUB-CONTRACTS	OTHER DIRECT COSTS	TOTAL COSTS
A. Compilation of CEM system QA Data - (daily and periodic checks, work requests, corrective action records, preventive maintenance records, monitor logs, audit/test reports, etc.)					
B. Back-up procedure for computer files and magnetic media					
C. Implementation of emissions and monitor record keeping and retrieval system					
D. Preparation of draft periodic reports					
1. Confirm unit and CEM system on-line/off-line periods					
2. Review DAHS alarms for effect on data quality					
3. Confirm or resolve issues or reason/corrective action codes					
4. Review emissions data for consistency with known performance					
5. Prepared edited emission summaries					
6. Prepared Data Assessment Report					
E. Internal review of draft report					
F. Revision and submission of report to agency					

Table F-1. Continued

9. Response Plan and Other Action - Sources will need to develop a plan for responding to emissions problems and CEM malfunctions. The costs for developing such a plan and responding to problems obviously will depend on the specific requirements and how the regulations are written and enforced. Costs may also be incurred in responding to agency questions or other follow-up actions. Guidance for estimating these costs is not provided here.

Table F-2. Summary of CEM System Cost Elements

ACTIVITY	ESTIMATED COST
1. Design/planning of the CEM System Program	
2. Selection of CEM System Equipment	
3. Purchase of Capital Equipment	
4. CEM System Installation	
5. Start-up and Performance Testing	
Subtotal Initial Costs	
6. Operation and Maintenance	
7. Quality Assurance	
8. Recordkeeping and Reporting Costs	
9. Response Plan and Other Action	
Subtotal Recurring Costs	
TOTAL Lifetime Costs	

Appendix G
Effects of Sample Matrix on Analyte Spike

Spiking the target analytes/surrogates into a flue gas matrix and calculating the recoveries can be challenging and can be influenced by experimental noise. To calculate the recovery of the analyte spikes, one must know the concentration of the target or surrogate compounds in the flue gas and whether these concentrations fluctuate with time. Calculating the recovery of the spiked analytes requires accurate knowledge of: 1) the flow rate of the spike gas, 2) the total sample flow rate (spike plus flue gas sample), 3) the concentration of the target/surrogate in the flue gas, and 4) the extent to which the concentrations vary with time. When flue gas concentrations vary significantly with time, an accurate calculation of the spike recovery may not be possible. A graphical representation of the effects of concentration variations on an analyte spiking experiment is given in Figure G-1.

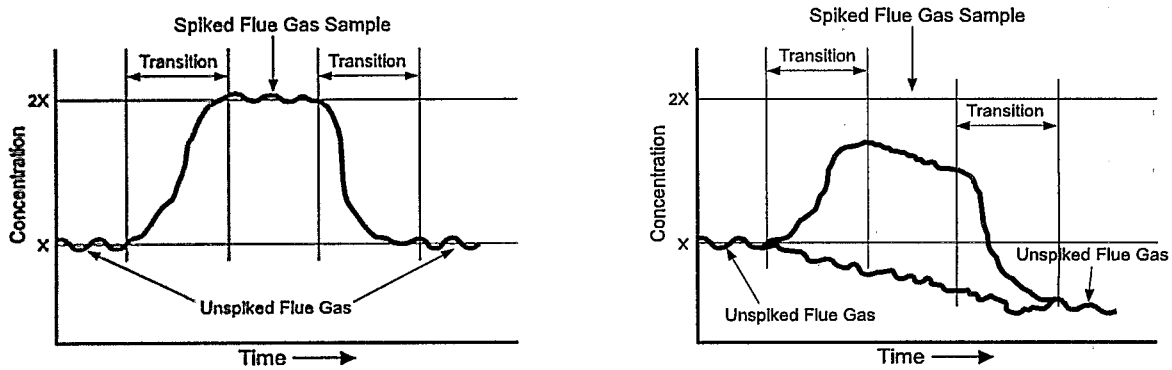

Figure G-1. Effects of concentration variations on analyte spiking experiments.

An ideal analyte spike concentration is one that approximates twice the flue gas concentration so that the spike most closely approximates the flue gas concentration. This may be difficult to accomplish without prior knowledge of the actual flue gas analyte concentrations. In practice, the spike concentration is constrained both by the available range of calibration standards and by the desire to limit the spike flow rate to less than 10 percent of the total sample flow rate so that sample matrix effects are not obscured by excessive dilution of the sample gas. In some cases, high level calibration standards may be diluted quantitatively with nitrogen to obtain spike gases that approximate the ideal analyte spike concentration.

Analyte Spike Calculations

The percent recovery (%R) of the spiked analytes are calculated as:

$$\%R = (S_m/C_e) \times 100 \qquad \text{Equation G-1}$$

Where:

S_m = Mean concentration of the analyte spiked flue gas samples (observed)

C_e = Expected concentration of the spiked samples (theoretical)

The expected concentration (C_e) of the spiked samples are calculated as:

$$C_e = D_f C_s + S_u (1 - D_f)$$ Equation G-2

Where:

D_f = Dilution Factor (Spike flow/Total flow)
total flow = spike flow plus flue gas sample flow
C_s = Cylinder concentration of spike gas
S_u = Native concentration of analytes in unspiked samples

The spike dilution factor may be confirmed by measuring the total flow and the spike flow directly. Alternately, the spike dilution can be verified by comparing the concentration of the tracer compound in the spiked samples (diluted) to the tracer concentration in the direct (undiluted) measurement of the spike gas. If SF_6 is the tracer gas, then:

$$D_f = [SF_6]_{spike} / [SF_6]_{direct}$$ Equation G-3

Where:

$[SF_6]_{spike}$ = The diluted SF_6 concentration measured in a spiked sample
$[SF_6]_{direct}$ = The SF_6 concentration measured directly

The bias is determined by calculating the difference between the observed spike value and the expected response (i.e., the equivalent concentration of the spiked material plus the analyte concentration adjusted for spike dilution). Bias is defined by EPA Method 301 (Section 6.3.1) as:

$$B = S_m - C_e$$ Equation G-4

Where:

B = Bias at spike level
S_m = Mean concentration of the analyte spiked samples
C_e = Expected concentration of the analyte in spiked samples

The bias (accuracy) is defined in terms of concentration where the recovery is expressed as a percentage of the expected concentration. For example, if a measurement technique gives a 2 ppm positive bias when attempting to measure 10 ppm, then the percent recovery would correspond to 120%.

*U.S. Government Printing Office: 1997 — 549-001/60149