



An Operator's Guide To Eliminating Bias In CEM Systems



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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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AIR AND RADIATION

It is a pleasure to transmit to you this *Operator's Guide to Eliminating Bias in CEM Systems*. Prepared for the U.S. Environmental Protection Agency by the internationally recognized continuous emission monitoring (CEM) systems expert Dr. James A. Jahnke, the *Guide* is an important tool for diagnosing and correcting the causes of measurement bias in CEM systems like those specified under the Acid Rain Regulations.

Experience gained through implementing the Acid Rain Program has shown that CEM operators can eliminate bias from monitoring systems by instituting and following appropriate installation, operation, and quality assurance and control procedures.

At the same time, Phase I certification test review has also revealed that many sources could use assistance in recognizing the physical and operational problems that produce systematic error and the remedies available to address those problems.

The *Operator's Guide* is designed to meet this need. Used as a reference document, the *Guide* makes it easier for CEM operators to improve monitor accuracy and meet regulatory requirements.

Sincerely,

A handwritten signature in black ink, appearing to read "Brian J. McLean".

Brian McLean, Director
Acid Rain Division



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An Operator's Guide To Eliminating Bias in CEM Systems

James A. Jahnke, Ph.D.
Source Technology Associates
Research Triangle Park, North Carolina

and

The Cadmus Group, Inc.
Raleigh, North Carolina

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Elliot Lieberman
Work Assignment Manager

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NOTICE

This is not an official policy and standards document. The opinions, findings, and conclusions are those of the author and not necessarily those of the U.S. Environmental Protection Agency. Every attempt has been made to represent the present state of the art as well as subject areas still under evaluation. Any mention of products or organizations does not constitute endorsement by the U.S. Environmental Protection Agency. This operator's guide is not an evaluation of the bias study the U.S. Environmental Protection Agency is to perform under 40 CFR 75.7.

PREFACE

The inclusion of the t-test for bias in the Acid Rain Regulations, 40 CFR Part 75, signaled a marked improvement in the capability to detect a significant source of measurement error that had previously remained hidden. The bias test provides an independent check of the full monitoring system, capable of determining whether systematic error is present in a monitoring system's measurements. It is a very forgiving test: it must be 97.5% confident that the error is not random in nature before it will describe the measurements as being biased. Field experience confirms that false positives are a rare occurrence when the bias test is properly performed.

At the same time, the capability to detect bias left environmental technicians and instrument operators with the often daunting job of, first, diagnosing the cause of the measurement bias, and, then, taking steps to correct it. This publication is intended to make that job easier.

It consists of two major components: A pull-out chart, entitled *Eliminating Bias in CEMS — A Checklist*, provides a comprehensive listing of the monitoring system problems that can cause systematic error. To make it easy for users to find problems associated with a particular type of monitor, the problems are grouped by monitoring system component type. A brief description and potential corrective actions are shown for each problem. Finally, the *Checklist* directs users to the appropriate pages in the accompanying *Operator's Guide*, where fuller descriptions of problems and remedies can be found.

The accompanying *Operator's Guide to Eliminating Bias in Monitoring Systems* is organized into eight chapters. Chapter 1 describes the history and the engineering and statistical basis for the bias test. Chapters 2–7 provide detailed descriptions of problems that can cause systematic measurement error and remedies that can be taken to address those problems. Each of the chapters is devoted to the problems associated with a different type of monitoring system component. The chapters begin with a table, excerpted from the *Checklist*, summarizing the problems to be discussed in that chapter. The problem areas covered are: Probe Location and Stratification (Chapter 2), Extractive Sampling Systems (Chapter 3), In-Situ Gas Monitoring Systems and Opacity Monitors (Chapter 4), Flow Monitors (Chapter 5), Gas Analyzers (Chapter 6), and Data Acquisition and Handling Systems (Chapter 7).

Chapter 8, the last chapter in the *Operator's Guide*, discusses elements that should be incorporated into ongoing Quality Assurance Programs to detect and prevent the problems that produce systematic error in monitor measurements. Each chapter ends with a list of references for further information on the subjects covered.

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CHAPTER 1

OVERVIEW: ACCURACY, PRECISION, AND BIAS IN CONTINUOUS EMISSION MONITORING SYSTEMS

CHAPTER 1

OVERVIEW: ACCURACY, PRECISION, AND BIAS IN CONTINUOUS EMISSION MONITORING SYSTEMS

1.1 BACKGROUND

Public concern with the environmental impact of acid rain resulted in Title IV of the Clean Air Act Amendments of 1990 which established emission standards for sulfur dioxide (SO₂) and nitrogen oxides (NO_x), the primary pollutants causing acid rain. To ensure that the emission standards were met, Title IV required continuous emission monitoring (CEM) systems to be put into operation at all affected utilities to measure SO₂ and NO_x as well as carbon dioxide (CO₂), diluent gases (CO₂ or oxygen, O₂), flue gas velocity, and opacity.

To limit the levels of SO₂ emitted, each source covered under Title IV is allotted a prescribed number of allowances, an allowance being the right to emit one ton of SO₂ per year. Because the total number of allowances issued by the U.S. Environmental Protection Agency (EPA) is strictly limited to the cap established in Title IV, the allowance allocation process provides the means to control SO₂ emissions and, consequently, acid rain.

Each year, the electric utilities are required to reconcile their total SO₂ emissions against the allowances held. The CEM systems, specified by Title IV, are instrumental accountants for the Acid Rain Program. Not only do they measure emissions, but they also allow utilities to track the consumption of allowances. In so doing, they provide the foundation for this extensive regulatory program.

A CEM system's continuous accounting of emissions allows the utility operator to determine the number of allowances used, the number available for the rest of the year, and the number that need to be acquired to operate for the remainder of the year. Because allowances have monetary value and can be bought, traded, auctioned, and otherwise transferred, it is imperative that CEM system data be accurate. Loss of allowances due to over-representation of emissions or inaccurate CEM systems are a concern to the utility. Under-reporting of emissions due to inaccurate systems are of concern to EPA. This document addresses such concerns by providing guidelines for obtaining accurate, unbiased CEM system data.

1.2 CEM SYSTEMS AND CERTIFICATION

A CEM system is composed of a number of subsystems: a gas monitoring system (which may use either extractive or in-situ sampling techniques and may include either a CO₂ or O₂ diluent correction monitor), a flow monitor, a transmissometer (opacity monitor), and a data acquisition and handling system (DAHS). An extractive system consists of a number of subsystems—the probe and conditioning systems and analyzers. A typical CEM system is shown in Figure 1-1.

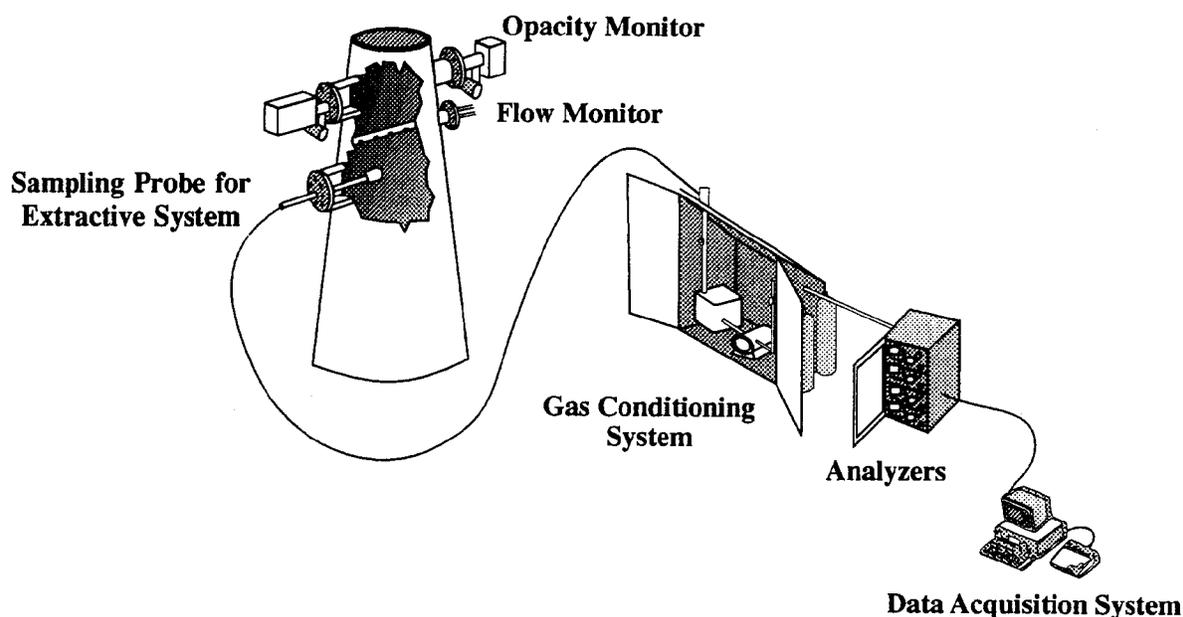


Figure 1-1. A Typical Continuous Emission Monitoring System

All of these components and subsystems work in concert to provide emissions data. There are, of course, many monitoring options (Jahnke, 1993). For example, in systems that extract gas from the stack, the gas can be cooled and the moisture removed or, alternatively, kept at an elevated temperature above the dewpoint and measured on a wet basis. Instead of measuring the extracted gas directly, it can first be diluted and measured using ambient air analyzers. Another option is to monitor the flue gas in-situ (i.e., directly in the stack or duct), without extraction.

The opacity and flow monitors shown in Figure 1-1 are in-situ monitors—the flue gas is monitored in-place and is not disturbed. The flow monitor is used here, in conjunction with gas concentration measurements, to calculate mass emission rates (i.e., in units of lbs/hr and tons/yr). The transmissometer monitors the flue gas opacity, which indirectly characterizes particulate matter emissions.

Although there are many types of systems, there is no one best system for all applications. CEM systems are application dependent. Regulatory conditions, stack gas composition, environmental and physical conditions, and even management practices can make one system better suited than another for a given application.

1.2.1 Performance-Based Standards

A CEM system is proven through its performance. If the installed system can meet established performance criteria, such as the standards for linearity, calibration drift, and accuracy, it can be approved for use as a regulatory continuous monitoring system. The U.S. EPA, the

International Standards Organization (ISO, 1989), and many European countries have adopted performance-based standards rather than design-based standards. In other words, the standard is not how the system is designed, but whether it works after it has been installed.

The U.S. EPA has established several sets of CEM performance specifications. These can be found in Title 40 of the U.S. Code of Federal Regulations (40 CFR) in Part 60 for New Sources, in Part 266 for facilities that burn hazardous waste, and in Part 75 for sources affected by the Acid Rain Program. Although these specifications are all similar, having evolved from the original Part 60 requirements, the 40 CFR 75 specifications are the most comprehensive and stringent. Because of the central role that Part 75 CEM systems play in the effective functioning of the Acid Rain Program allowance market, the CEM data must be as accurate and precise as possible.

1.2.2 Relative Accuracy Test Audit

A principal performance testing procedure for Acid Rain CEM systems is the relative accuracy test audit (RATA). The RATA is a comparative evaluation of the CEM system performance against an independent reference method. A reference method can be either (1) a manual wet chemistry method, where, for example, gas is extracted from the stack and bubbled through an absorbing solution which is then analyzed in a chemical laboratory, or (2) an instrumental method, where gas is extracted from the stack and analyzed directly by suitably calibrated analyzers. Under the Acid Rain Program, the applicable reference methods are Method 2 (reference method for determination of stack gas velocity and volumetric flow), Method 6 (manual reference method for SO₂) or Method 6C (instrumental reference method for SO₂), and Method 7 (manual method for NO_x) or Method 7E (instrumental method for NO_x).

Specifications for both the manual and instrumental reference methods are found in 40 CFR 60 Appendix A. Figure 1-2 illustrates a typical RATA, using a monitoring van with automated test equipment.

In a RATA, a minimum of nine sets of paired monitoring system and reference method test data are obtained. A tester may perform more than nine sets of reference method tests and may reject up to three data sets, as long as the total number of runs used in calculating test results is equal to or greater than nine. Data from the RATA are used to determine both the relative accuracy and bias, if any, of a CEM system.

1.3 ACCURACY AND BIAS — A CONCEPTUAL VIEW

Technically, the accuracy of a measurement refers to the degree of agreement between the measured value and a true value. In source measurements, as in physical science in general, the true value of a physical parameter is rarely known. Instead, an "accepted" true value is generally used for comparison against the CEM system measured values. In source testing, the "true" value is assumed to be that value determined by the EPA Reference Method.

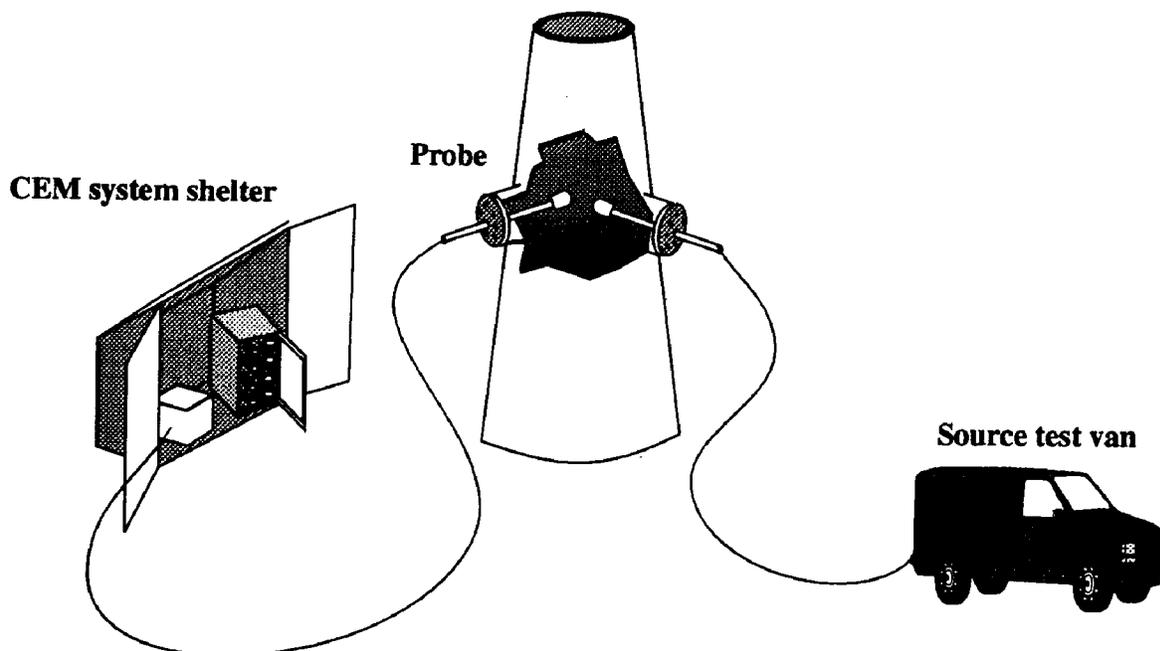


Figure 1-2. Relative Accuracy Test Audit Using Instrumental Reference Methods

1.3.1 Relative Accuracy Test

Relative Accuracy is a regulatory statistic that expresses CEM accuracy in relative terms, i.e., it quantifies the deviation of the CEM from the reference method relative to the emission levels occurring at the time of the RATA. Derived from the paired data measurements (Natrella, 1963) obtained during the RATA, it is expressed as a percentage of the average of the emission levels encountered during the RATA. This calculation is in contrast to most engineering practice, which expresses accuracy as a percentage of span. As such, relative accuracy is closely associated with the source emission levels occurring at the time of the test, rather than with instrument span.

The relative accuracy is calculated using the following expression:

$$RA = \frac{\bar{d} \times \% cc}{\overline{RM}} \times 100 \quad (\text{Eq. 1-1})$$

To calculate \bar{d} , the absolute value of the mean difference between data pairs, the arithmetic difference between the reference method and the CEM system measurements for each data pair is first calculated:

$$d_i = RM_i - CEM_i \quad (\text{Eq. 1-2})$$

where d_i is the difference between a reference method value and the corresponding monitor or CEM system value for the i^{th} test run.

The mean difference is then calculated using the expression:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^n d_i \quad \text{(Eq. 1-3)}$$

where

n = the number of data pairs.

The absolute value of \bar{d} is then used in Eq. 1-1. In calculating the sum of the differences between the data pairs, it is important to note that the signs of the differences are retained (that is, the absolute value is taken of the total summation, not the individual d_i values).

The confidence coefficient is determined from the following expression:

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}} \quad \text{(Eq. 1-4)}$$

where

$t_{0.025}$ = a statistical parameter used to calculate *cc* for a given number of data pairs (Table 1-1).

Table 1-1. t-Values

| n-1 | $t_{\alpha=0.025}$ |
|-----|--------------------|
| 8 | 2.306 |
| 9 | 2.262 |
| 10 | 2.228 |
| 11 | 2.201 |
| 12 | 2.179 |
| 13 | 2.160 |
| 14 | 2.145 |

S_d = the standard deviation of the differences of the data pairs obtained during the relative accuracy test.

$$S_d = \left[\frac{\sum_{j=1}^n (d_j)^2 + \left[\frac{\sum_{j=1}^n d_j}{n} \right]^2}{n+1} \right]^{\frac{1}{2}} \quad \text{(Eq. 1-5)}$$

The confidence coefficient is a measurement of the uncertainty in the calculation of \bar{d}^* : Because the relative accuracy determination is made from a finite set of data, there is a probability that \bar{d} could be larger or smaller. cc^* represents the largest variation in \bar{d}^* , which we would expect to see 97.5% of the time (i.e., it would only be exceeded 2.5% of the time).

\overline{RM} , the term appearing in the denominator of Eq. 1-1, is the arithmetic mean of the reference method values:

$$\overline{RM} = \frac{1}{n} \sum_{j=1}^n RM_j \quad \text{(Eq. 1-6)}$$

In Part 75, the relative accuracy, calculated from concentration units (ppm or percent), for SO₂ and CO₂ monitors must be 10% or less. For an NO_x monitoring system, the relative accuracy must be 10% or less, calculated from units of lbs/mmBtu (ng/Joule) obtained from both NO_x and diluent (CO₂ or O₂) measurements. For flow monitors, the relative accuracy, derived from measurements in units of standard cubic feet per hour, must be 15% or less.

Figure 1-3 offers a graphical representation of the underlying frequency distributions inferred from two hypothetical relative accuracy test audits (denoted Case A and Case B). The graphs show the uncertainty about the estimate of mean differences for the two sample RATAs. Each distribution shows the range and variability in the mean difference that can be inferred from the RATA measurements. The horizontal axis displays the mean difference (\bar{d}) found using Eq. 1-3, where CEM system measurements are compared to the "accepted" true values determined by the reference method.

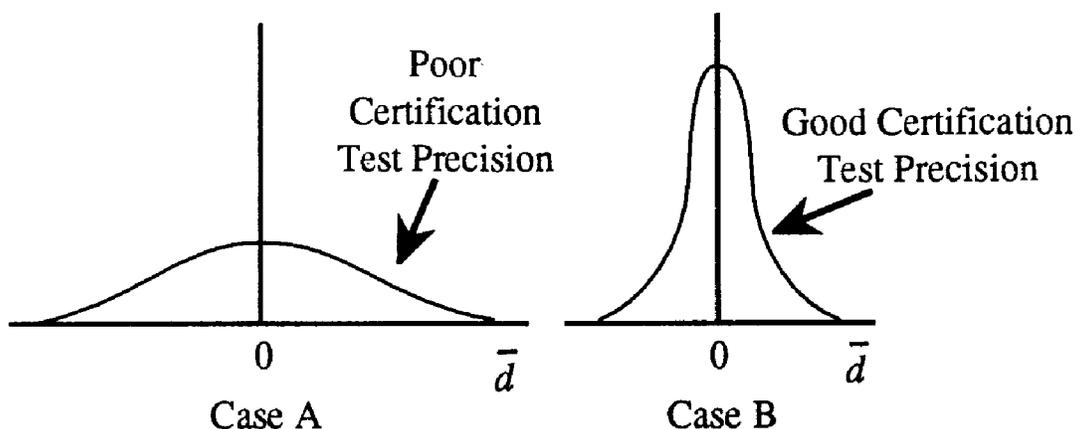


Figure 1-3. An Illustration of Precision in Two Hypothetical Relative Accuracy Test Audits

For illustrative purposes in both Case A and Case B, the difference between the CEM and reference method on average is assumed to be zero. (This is represented by each distribution being centered at the zero point on the horizontal axis.) Thus, in both situations bias is not a factor. However, the comparative steepness of two distributions reveals striking differences in the precision of the differences between the CEM system and reference method prevailing during the RATA. In Case A, the curve is squat, indicating that the values of d_i varied appreciably from run to run, to produce a wide variation in \bar{d} . It was not possible to reproduce the data well. Such a situation could possibly indicate an erratic CEM system, poor reference method testing, or both. In contrast, the curve in Case B is sharp, indicating that the difference between the reference method values and CEM values were nearly the same for each of the nine test runs used to calculate \bar{d} . The data were reproducible. The instruments displayed a high degree of precision. The squatness and sharpness of the two curves is captured by cc^* in the numerator of Eq. 1-1.

1.3.2 Bias

The relative accuracy test, used in CEM certification and performance testing, captures the degree of relative imprecision in CEM measurements, but it does not differentiate systematic error from random error. Prior to the promulgation of 40 CFR Part 75, the relative accuracy test alone was used to limit both imprecision (random error) and measurement bias (systematic error).

There is a problem, however, in only using the relative accuracy specification. For example, if a CEM systematically reads 9% low relative to the reference method, it could still pass a 10% relative accuracy standard even though the data subsequently reported to the agency would be consistently 9% low. This situation is particularly serious in the Acid Rain Program, because such a possibility would both jeopardize the achievement of the Program's mandated emission limits and undercut the program-wide uniformity of emission measurements, thereby calling into question the true valuation of SO_2 allowances.

To address this situation, 40 CFR Part 75 tightened the relative accuracy standard to 10% and subjected RATA data to a bias test, specifically designed to detect systematic error.

1.3.3 Bias Test

Besides being used to calculate relative accuracy, the paired RATA data are also used to determine if statistically significant systematic error (low bias) is manifested in the CEM measurements. A t-test is applied to the paired differences to test the hypothesis that differences between the CEM and reference method are not statistically different from zero. If the mean difference of the measurements as found in Eq. 1-3 exceeds the confidence coefficient as found in Eq. 1-4, then the hypothesis is rejected. According to well-established principles from classical statistics, if the mean difference exceeds the confidence coefficient then we can be 97.5% confident that the measurement difference was not a random occurrence, i.e., that the difference was due to systematic, not random, error. Thus low bias is considered to be present if

$$\bar{d} > *cc* \tag{Eq. 1-7}$$

This expression merely states that systematic error is considered to be present if on average the CEM measurements are so far below the reference method measurements as to lie outside the confidence limits. That is, they are so low that the \bar{d} derived from the RATA data falls in a zone where classical statistics predicts with 97.5% confidence that \bar{d}_{true} will not occur. In other words, the CEM system is reading so low relative to the reference method that we are 97.5% confident that the system is biased low (Figure 1-4).

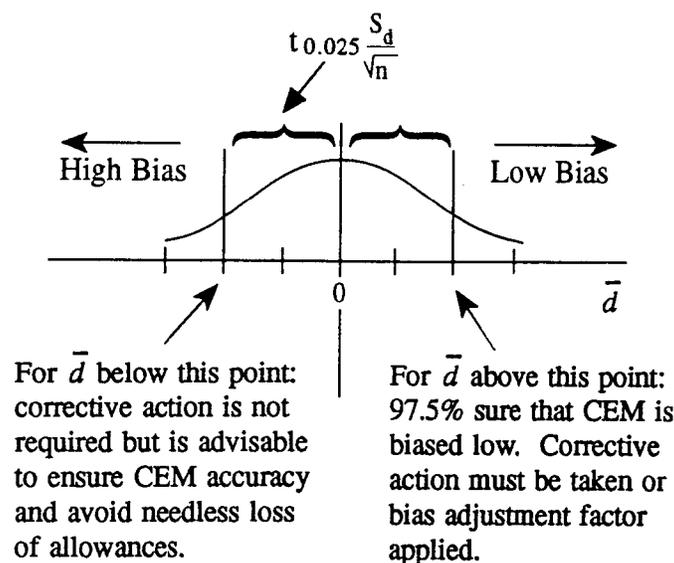


Figure 1-4. t Distribution for a RATA, Showing when Bias Occurs

Equation 1-7 is basically an expression of the one-tailed t-test. By using it, there is at most a 2.5% probability of mistakenly detecting low bias when there really is none. It is important

to note that the bias test is very forgiving. A CEM system is said to be biased only when there is less than a 2.5% probability that the low readings occurred by chance.

The bias test is quite useful in detecting CEM system problems. Although the Part 75 requirements do not allow low-biased systems, high-biased systems are permitted [as long as the relative accuracy specification (10% for SO₂ and NO_x, 15% for flow) is still met]. Obviously, although a high-biased system is allowed under the Acid Rain Regulations, it would result in the loss of allowances and would not be advantageous to a source owner. Therefore, a CEM system owner should apply the test to check for **both** low and high biases between the CEM system and reference method. Ideally, the cause of the bias should be detected and remedied to give the most accurate data possible.

1.4 ELIMINATING BIAS AND THE BIAS ADJUSTMENT FACTOR

When bias is detected, two options are provided under Part 75. The preferable course of action is to determine the cause of the bias and eliminate the problem. This *Guide* is specifically designed to assist in this process by providing guidance in diagnosing and remedying the sources of measurement bias.

Alternatively, Part 75 provides a regulatory remedy. To compensate for the systematically low CEM measurements detected during the RATA, a bias adjustment factor can be derived from the RATA data and applied to subsequent CEM measurements. A CEM system owner is allowed the option of applying a bias adjustment factor if low bias is detected and the cause of the bias is not corrected. The bias adjustment factor is given in Eq. 1-8:

$$BAF = 1 - \frac{\bar{d}^*}{\overline{CEM}} \quad \text{(Eq. 1-8)}$$

where

BAF = bias adjustment factor

\bar{d}^* = absolute value of the arithmetic mean of the difference obtained during the failed bias test using Eq. 1-3

\overline{CEM} = Mean of the data values provided by the monitor during the failed bias test.

The magnitude of the bias adjustment factor is such that if the original CEM data were multiplied by the BAF, the average of the resulting values would exactly equal the average of the reference method readings and, consequently, \bar{d}^* would equal zero. Using Eq. 1-9, this factor is applied to all subsequent CEM system data for the measured parameter until the next relative accuracy test has been performed.

$$CEM_i^{Adjusted} = CEM_i^{Monitor} \times BAF \quad (\text{Eq. 1-9})$$

where

$CEM_i^{Adjusted}$ = Data value, adjusted for bias, at time i

$CEM_i^{Monitor}$ = Data (measurements) provided by the monitor at time i .

If the CEM system passes the bias test at the time of the next relative accuracy test, no adjustment would then be required. If the system fails, a new bias adjustment factor must then be calculated and applied unless the cause of the bias is determined and corrected.

When bias is detected but not corrected, CEM system bias adjustment factors are typically on the order of 3 to 4% of the CEM system measurement values. Before purchasing a CEM system, it should be decided by the user whether this level of adjustment would be acceptable. If not, the CEM system contract should specify to the CEM system vendor that bias-free or less biased Part 75 systems are to be provided.

It must be noted that it is always preferable from a measurement standpoint to eliminate the sources of bias in a CEM system rather than resort to the regulatory remedy provided by the bias adjustment factor.

1.5 SOURCES OF ERROR IN CEM SYSTEMS

Systematic and random errors can occur in all of the subsystems and components of a CEM system. It is left to the skill and experience of the CEM system manufacturer, integrator, and operator to minimize biases and obtain the best possible accuracy and precision. It is then the responsibility of the CEM system owner and operator to maintain the system to specified levels of accuracy and precision.

This guideline document will discuss sources of CEM system bias and possible methods of detecting and correcting bias problems. Specifically, bias problems associated with the following, will be discussed:

1. Sampling location and stratification
2. Dilution-extractive system biases
3. Source-level extractive biases
4. In-situ gas and flow monitor biases
5. Pollutant and diluent analyzer biases
6. Data acquisition and handling system problems

This document cannot identify all CEM system problems and sources of bias as many are system specific. However, it can point out some of the primary sources of systematic error that can be addressed when evaluating CEM system performance.

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CHAPTER 2

BIAS DUE TO PROBE LOCATION AND STRATIFICATION

Chapter 2 Highlights

Probe Location and Stratification Problems

| Problem | | Corrective Actions | Page Refs |
|---------------------------------|---|--|------------|
| Name | Description | | |
| Stratification — All Types | Gas stratification and flow stratification produce unrepresentative sampling and bias measurements during Relative Accuracy Test Audit. | <p>Find unstratified locations if at all possible.</p> <p>Use fans or gas reinjection to solve gas stratification problems.</p> <p>Use straightening vanes or baffles to solve flow problems.</p> | 2-9 |
| Stable Stratification Patterns | Stratification is present but pattern does not vary over time, i.e., with load or process changes. | <p>Sample at a point representative of the area of measurement.</p> <p>Monitor on a path representative of the area of measurement.</p> | 2-9, 2-10 |
| Varying Stratification Patterns | Stratification is present and pattern varies as plant's operating conditions change. | <p>Calibrate the monitored values to the reference values determined over the range of variation (e.g., different load/process conditions).</p> <p><u>For point sampling systems:</u> Extract or monitor at multiple points.</p> <p><u>For path sampling systems:</u> Monitor on paths less sensitive to variation.</p> <p>Monitor on multiple paths on the cross-section.</p> | 2-10, 2-11 |

CHAPTER 2

BIAS DUE TO PROBE LOCATION AND STRATIFICATION

2.1 INTRODUCTION

One of the principal sources of bias in CEM system certification is associated with sample probe location and gas stratification in the duct or stack. Because of the way in which a relative accuracy test is conducted, the reference method and CEM system will usually measure from two different sample points (Figure 2-1).

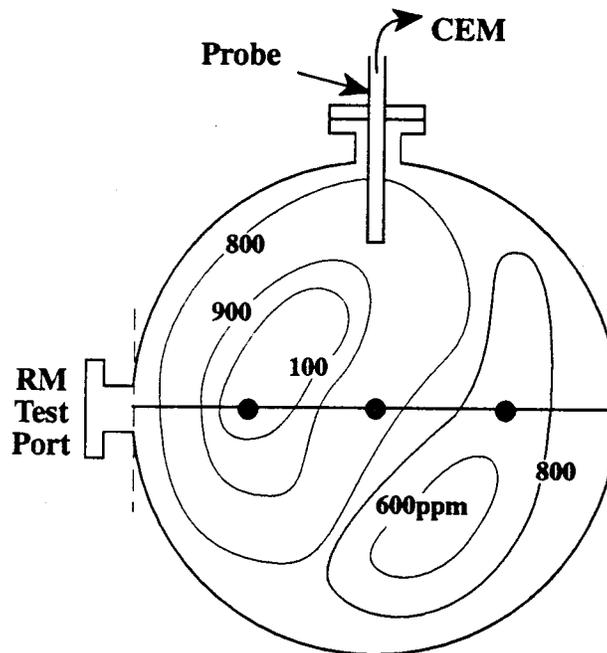


Figure 2-1. Stratification and Reference Method Testing in a Stack

The figure shows that, depending on the stratification profile, the reference method sample taken at the three required sample points shown may differ from the sample taken at the single point by the CEM system. This discrepancy may represent a constant error if the stratification profile does not change with load or plant operating conditions. However, if the profile changes with operating conditions, "blind" application of the regulatory remedy embodied in a single bias adjustment factor, or an engineering "fix" provided by a CEM correction factor, may not result in representative emissions data.

For Part 75 Acid Rain CEM systems, two types of flue gas stratification are of concern: (1) gas concentration stratification and (2) velocity stratification. Because SO₂ emission allowances

are expressed in terms of mass/time (e.g., lbs/hr or tons/yr), as calculated in Eq. 2-1, both an SO₂ and a flow (velocity) monitor are necessary:

$$pmr = c_w A_s L_w \quad \text{(Eq. 2-1)}$$

where:

pmr = pollutant mass rate (lbs/hr, tons/yr)

c_w = pollutant gas concentration determined on an actual, wet basis (lbs/ft³, ppm)

A_s = stack or duct cross-sectional area

L_w = flue gas velocity

Further complexity arises when the velocity stratification and gas stratification profiles are not identical over the cross-section. In such situations, the expression of Eq. 2-1 is only an approximation to the general expression given in Eq. 2-2:

$$pmr = \int_A c_a L_a da \quad \text{(Eq. 2-2)}$$

where:

c_a = the gas concentration in the area increment da

L_a = the flue gas velocity in a direction normal to the area increment da

da = an area increment

An example of a situation where both the gas concentration and flue gas velocity are stratified is given in Figure 2-2.

Accurate monitoring of the pollutant mass rate under such conditions can be very difficult. Either multi-point sampling systems, line averaging systems, or other methods may be necessary to obtain measurements that approximate the "true value."

Additional problems in stratification result when the flow monitoring system is not measuring in the same manner as the gas monitoring system. For example, an ultrasonic sensor may measure a line-averaged value, whereas the gas extractive system may obtain a sample from only one point.

Thus, several biases due to stratification may enter into the reported pollutant mass rate. Such biases, coupled with the biases introduced by the choice of reference method sampling points (as illustrated in Figure 2-1), may make it difficult to certify a CEM system within the relative accuracy specifications, or for it to pass the bias test without a careful diagnosis of the sources of bias and application of remedies as described below.

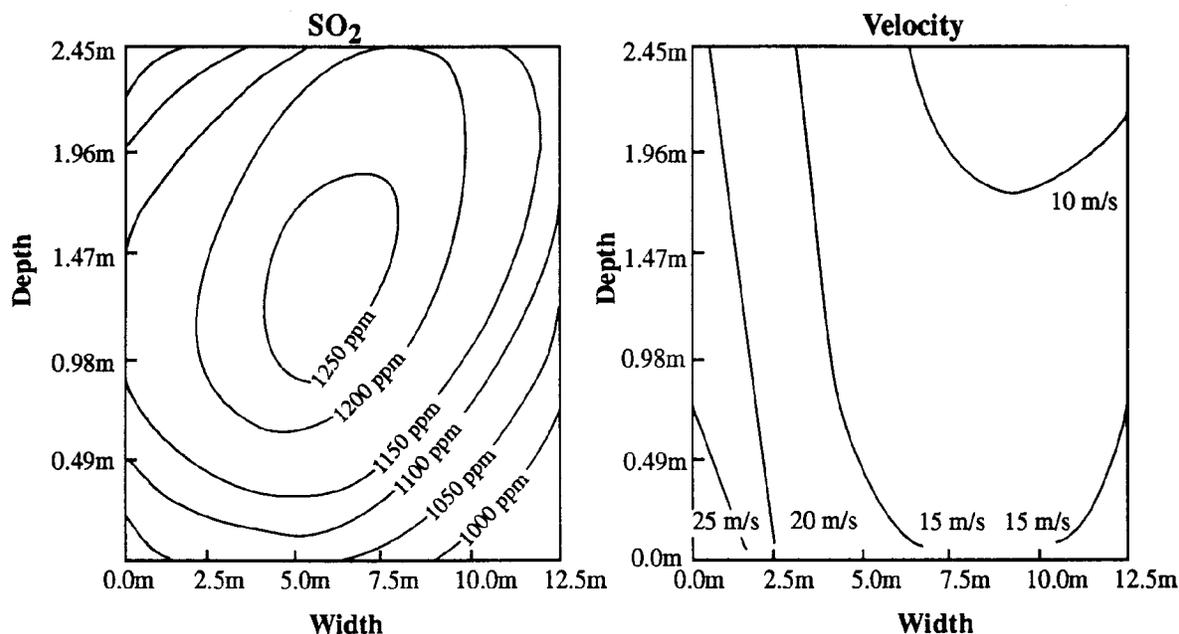


Figure 2-2. Stratification in Gas Concentration and Flue Gas Velocity (Gregory et al., 1976)

2.2 REFERENCE METHOD TRAVERSE POINTS AND SAMPLING LOCATIONS

As noted above, the reference method testing for gas concentration measurements is performed on a three-point traverse rather than at a single point in the stack or duct (40 CFR 60 Appendix B PS2 §3.2). However, it should also be noted that these are "minimum" requirements and that the prevailing requirement is instead:

"Select traverse points that assure acquisition of representative samples over the stack or duct cross section" (40 CFR 60 Appendix B PS2 §3.2), and

"Select traverse points that (1) ensure acquisition of representative samples of pollutant and diluent concentration, moisture content, temperature, and flue gas flow rate over the flue cross section..." (40 CFR 75 Appendix A § 6.5.6).

The minimum requirement for pollutant gas concentration measurements in PS2 §3.2 specifies that samples are taken on a three-point traverse on a measurement line that passes through the centroid of the stack or duct and in the direction of any expected stratification. For a measurement line less than 2.4 m, samples are taken at points that are located 16.7, 50, and 83.3% on the line (Figure 2-3a).

For larger ducts or stacks with a measuring line greater than 2.4 m and where stratification is not expected, sampling points are specified at 0.4, 1.2, and 2.0 m (Figure 2-3b). (This second

option is not allowed after wet scrubbers or where two gas streams with different pollutant compositions combine.) Samples are to be taken within 3 cm of these points.

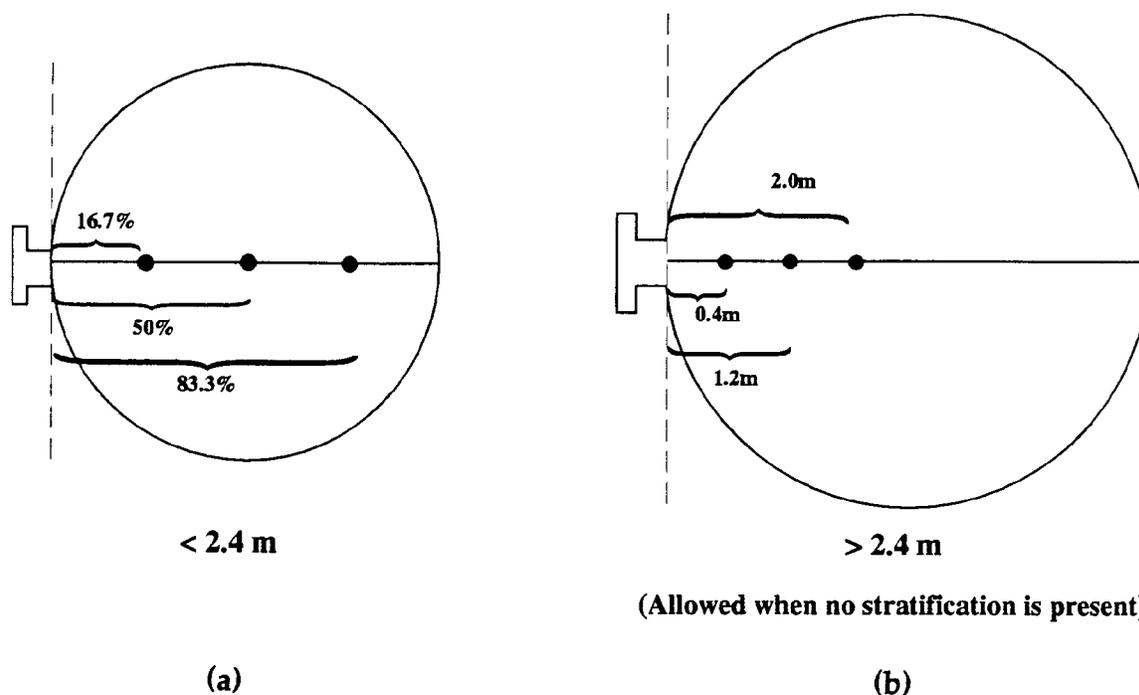


Figure 2-3. Gas Sampling Reference Method Traverse Points Specified in 40 CFR 60 Appendix B

In contrast to the gas sampling traverse points, velocity traverse points are those specified by EPA Reference Method 1. Here, a minimum of 12 or 16 points (depending on the sampling location) are to be tested.

Reference method sampling locations are the same as those specified for CEM systems, which are at least two equivalent diameters downstream from a disturbance, such as an elbow, a control device, or an expansion or a contraction and one-half equivalent diameter upstream from a disturbance or the effluent exhaust. Such criteria are generally not difficult to meet when the CEM system is installed in a stack; it is often difficult, however, to find two diameters of straight run in ductwork.

2.3 GAS AND FLOW STRATIFICATION

Flowing gases are generally well-mixed, but stratification can occur when there are differing temperatures or when dissimilar gas streams intersect. Figure 2-4 illustrates a number of conditions where gas concentration stratification may occur.

Air leaking into a duct, the combining of two-process gas streams into a stack, or the reintroduction of scrubber by-pass gas into a flue can all result in such stratification. In combustion sources, air in-leakage occurs usually near the preheaters. Columns of gas with high, unmixed NO_x concentrations have even been observed after burners. The problem is further complicated because this stratification is not only spatial, but can also change temporally, as a function of time. As process-load or other conditions change, the gas or flow distributions can also vary as a function of time as well as spatially.

Numerous examples of gas stratification patterns can be found in the literature. The work of Zakak et al. (1974) gives a detailed discussion of these problems.

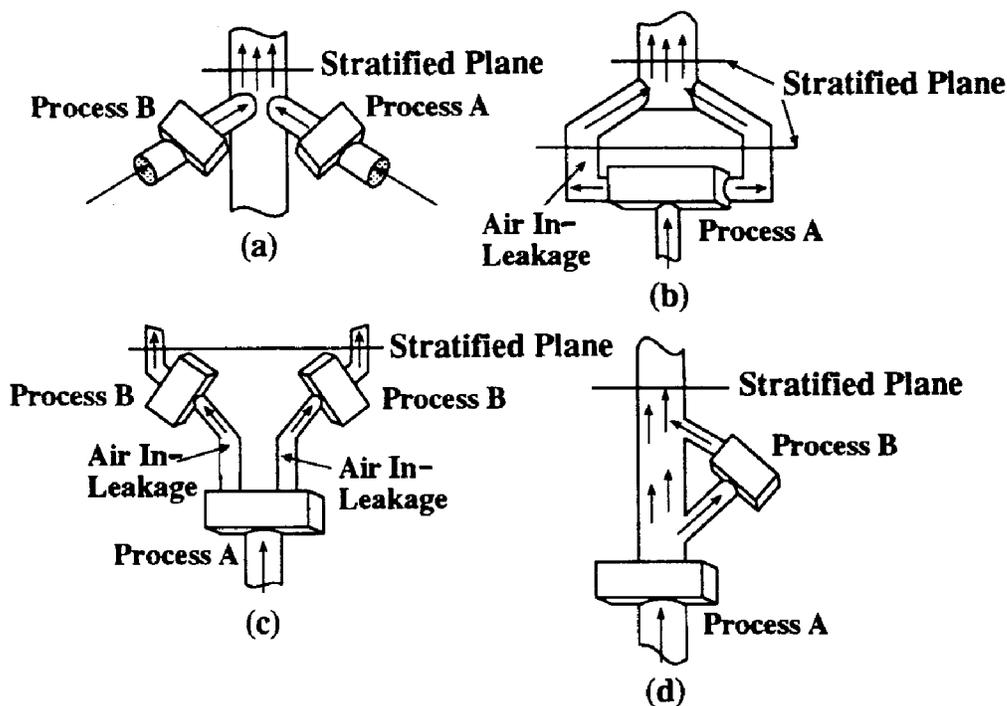


Figure 2-4. Conditions Under Which Gas Concentration Stratification May Occur (after Zakak et al., 1974)

[Combining two gas streams into a stack (a, b, d), air in-leakage (b, c), and reintroduction of scrubber by-pass gas into a flue (d).]

Velocity stratification is expected even in a fully developed flow profile, due to the effects of the stack walls on the moving flue gas. Support struts in ductwork may also cause problems in flow measurements. Eddies formed around the struts may disturb the sensing elements of a velocity monitor, or they can physically obstruct the measurement path or point.

The presence of cyclonic flow is particularly problematic, and sampling should be avoided where cyclonic flow is present. Gas streams entering tangentially to a stack can produce cyclonic, swirling flow (Figure 2-5). Velocity monitors can be particularly sensitive to flow direction.

Differential pressure sensor systems will sense different impact pressures depending on the angle of the flow relative to the impact pressure opening. Ultrasonic flow sensors can miss "pitched" gas streams or improperly weight the velocity across a line average. For this reason, it is specifically recommended in Part 75 that sampling locations be avoided where swirling flow is present.

2.4 QUANTIFYING THE DEGREE OF STRATIFICATION

It should be obvious from the above discussion that, based merely on duct diameter criteria, gas concentration or velocity stratification may or may not be present in a stack or duct. The criteria of 8- and 2-duct diameters or 2- and $\frac{1}{2}$ -duct diameters are regulatory constructs. In the case of gas stratification caused by temperature differentials, the gas may not become well-mixed even beyond 40-duct diameters.

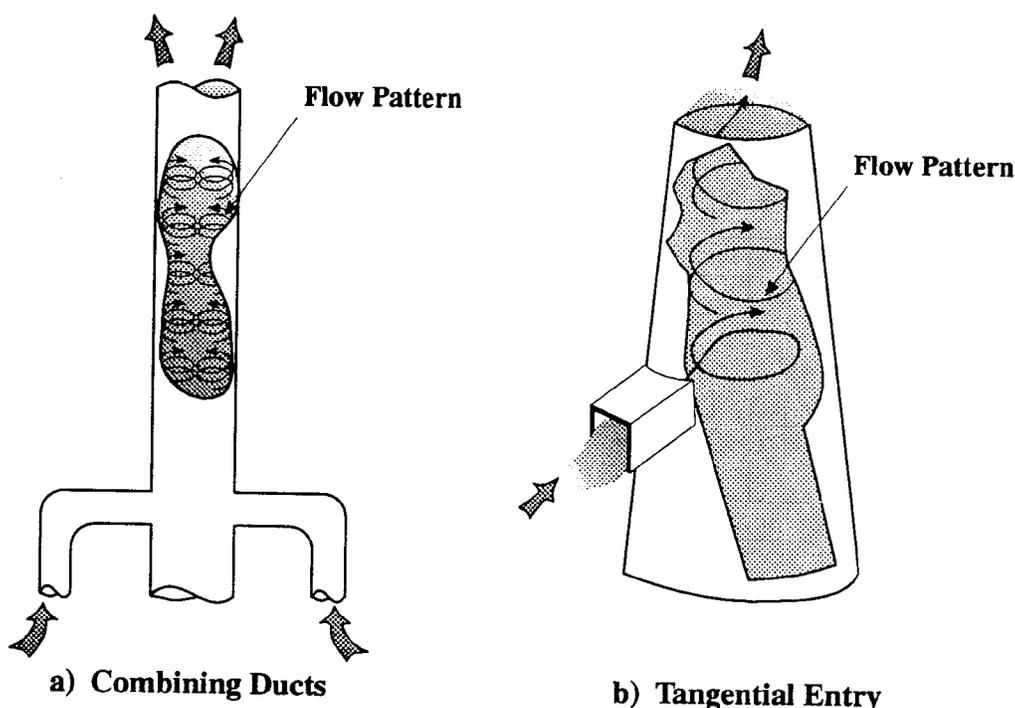


Figure 2-5. Conditions Under Which Flow Stratification or Cyclonic Flow Conditions May Occur

The degree of stratification in a duct or stack can be quantified. One method of quantification has been proposed (U.S. EPA, 1979) that involves traversing the stack or duct and obtaining gas concentration values. An example scenario for a rectangular duct would be to sample at nine sampling points of a balanced matrix. The degree of stratification at each sampling can be calculated as:

$$\% \text{ Stratification at point } i = \frac{(c_i \text{ \& } c_{ave})}{c_{ave}} \times 100$$

where

c_i = concentration of the pollutant at point i

c_{ave} = average of the nine concentrations.

The sampling plane is said to be stratified if any value is greater than 10%.

When performing a stratification test, it is good practice to sample at a single point over the entire sampling period (e.g., Elam and Ferguson, 1985). This procedure is easily done using an instrumental technique. The data obtained can be used to determine if gas concentrations are changing as a function of time as well as spatially. If the concentration varies at the point over the sampling period, the traverse data will be difficult to interpret. Ideally, gas stratification studies should also be sampled isokinetically (i.e., sampling at a rate equal to the flue gas velocity) (Gregory et al., 1976), since over-isokinetic sampling of the flue gas may upset stratification patterns.

Although the quantitative determination of stratification may be useful in discussing the severity of a stratification problem, concentration or velocity isopleths (lines connecting points having the same value) are much more useful. Profiles such as those shown in Figure 2-1 and Figure 2-6 (below) can assist in siting both gas and velocity monitoring systems.

In circular stacks, stratification testing is normally conducted on the two perpendiculars of the cross-section specified by EPA Reference Method 1. Although this procedure may give reasonable values for area averages, it is often difficult to construct reasonable isopleths from the data. A modification of the EPA equal area procedure may be necessary to construct contours such as those shown in Figure 2-6. Because the object is to construct the isopleths and not to obtain an equal area average, the central point and points on diameters other than the two perpendiculars should be sampled to more completely define the stratification patterns.

Numerous problems can occur in the measurement of flow when attempting to characterize the profile, especially when the flow is nonparallel or cyclonic. Proper use of the S-type pitot tube, specified in EPA Reference Method 2, requires that the direction of gas flow be perpendicular to the plane of the impact pressure opening. EPA Reference Method 1 gives procedures that can be used to verify whether cyclonic flow is present and also provides procedures for measuring the non-axial components of flow, using a directional probe (3-dimensional pitot tube). The draft Method 2F contains additional procedures for measuring under nonparallel flow conditions. These methods should be considered before developing the stratification test plan and conducting the test.

Stratification tests are difficult to perform well and are costly if a complete characterization of pollutant flow distributions is needed. Also, many CEM systems are installed in new plants and must be on-line at the time of plant start-up. Because sampling locations are decided upon during plant design and construction, it is usually not possible to conduct stratification tests to guide CEM installation decisions in new plants. However, in such cases, computer modelling studies can be conducted from the proposed plant design. These studies have shown good agreement with testing conducted after construction (Gielow and McNamee, 1993). An alternative to computer modelling is cold-flow modelling, testing flows in Plexiglas constructions of the intended ductwork.

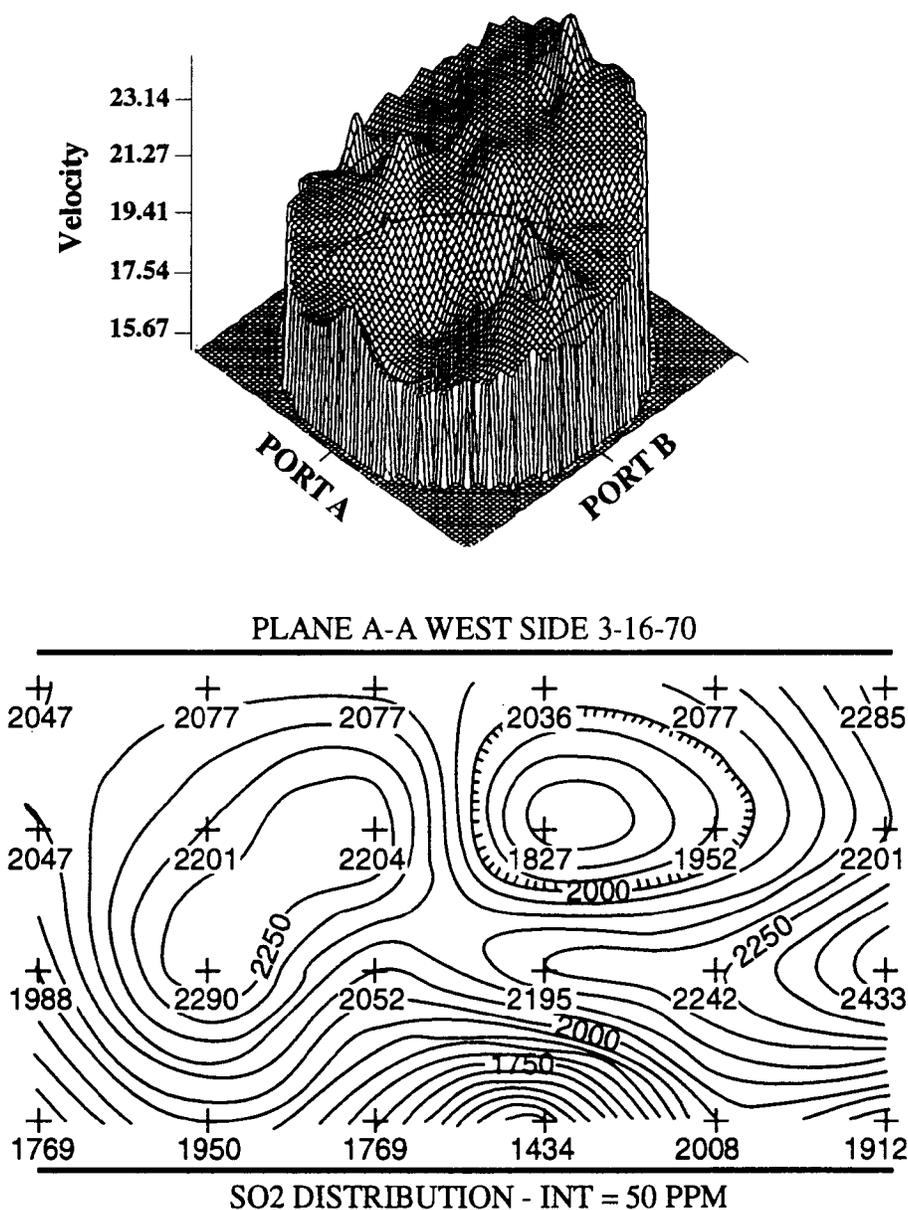


Figure 2-6. Velocity and Gas Concentration Profiles

2.5 MINIMIZING BIAS IN STRATIFIED GAS STREAMS

If at all possible, monitoring in stratified gas streams should be avoided. Other possible locations should be considered and tested to determine the presence of more uniform gas flows and concentrations. Alternatively, straightening vanes or baffles can be used to solve flow problems; fans or gas reinjection (Zakak et al., 1974) may solve gas stratification problems. Such engineering solutions may, however, require more power to move the flue gas through the ductwork and consequently add to plant operating costs. If stratification is present, either in the stack or in ductwork, a number of options are possible for minimizing bias between the monitoring method and reference method. These are listed in Table 2-1.

Table 2-1. Methods for Minimizing Bias due to Stratification

| | |
|---|---|
| For stable stratification patterns: | |
| C | Sample at a point representative of the area measurement. |
| C | Monitor on a path representative of the area measurement. |
| C | Calibrate the monitoring system to the reference method values. |
| For varying stratification patterns: | |
| C | Calibrate the monitored values to reference method values determined over the range of variation (e.g., different load/process conditions). |
| C | For point monitoring systems, extract or monitor at multiple points on the cross-section. In severely stratified situations, monitor at all Reference Method 1 traverse points. |
| C | For path monitoring systems, monitor on paths less sensitive to the variation. |
| C | For path monitoring systems, monitor on multiple paths on the cross-section. |

2.5.1 Stable Stratification Patterns

If the stratification pattern is stable over time, as load or process conditions change, two principal options are available. The simplest option requires examining the stratification pattern to determine a point or path that is representative of the reference method emissions.

The second option is to calibrate the monitoring system to the reference method values. This practice is common with manufacturers of flow monitoring systems, who generally require a "pre-RATA" to be conducted before the actual certification. Essentially, the manufacturer determines the bias beforehand and factors it into the instrument response. Although such empirical calibrations are common in flow monitoring, they are not frequently made in gas monitoring systems.

This procedure of correcting for bias before the certification test may appear to be circumventing the performance specification criteria, particularly the bias criteria of 40 CFR 75 Appendix A §7.6.4 and 7.6.5, which do not provide a bias adjustment factor for reducing positive bias. However, it must be remembered that EPA CEM system performance specifications on the whole are performance-based, not designed-based. It does not matter if a correction factor, correction algorithm, or random number generator is used within the system itself, as long as the same internal computational routine continues to be used unmodified for certification, normal emissions measurement, and routine quality assurance/quality control (QA/QC) checks. If the resulting system can meet all of the performance specifications for calibration error, linearity, relative accuracy, etc., during a certification test and during subsequent required periodic QA/QC testing, the system will be approved.

2.5.2 Varying Stratification Patterns

The problem of obtaining representative measurements can become more complicated when the stratification pattern varies under plant operating conditions. A typical situation occurs when two ducts exhaust into a single stack, but the volumetric flow rates of the gas through each duct vary under different plant operating conditions. Flow profiles downstream of bends are also expected to vary with load. In such cases, a "representative" sampling point or monitoring path may not exist. In others, it may be possible to program a calibration curve (Stahlschmidt, 1992) into the monitor response.

If it is necessary to monitor under such conditions, a "brute force" approach can be taken to achieve system certification. Basically, if a system is designed to sample at the traverse points of the reference method, then it should be able to meet the relative accuracy criteria. For gas monitoring, a minimum of three sample probes or a tube with multiple sampling ports could be used for this purpose.

In flow monitoring, differential pressure-sensing systems using probes with sensing ports at the reference method traverse points solve this problem quite easily. Similarly, path monitors can traverse the stack or duct over multiple paths to monitor the cross-sectional area more effectively (Lynnworth et al., 1992; Kearney, 1993). However, it may be necessary to program computational routines into the instrument to correct the line averages to an area average in path monitoring systems.

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CHAPTER 3

SOURCES OF BIAS IN EXTRACTIVE CEM SYSTEMS

Chapter 3 Highlights

Sampling System Problems — Extractive CEMS

| Problem | | Corrective Actions | Page Refs |
|---|--|---|------------|
| Name | Description | | |
| Probe Problems — Source Level Systems | | | |
| Plugging | Particulate matter clogs sampling probe. | Blowback. Increase filter surface area. | 3-3, 3-4 |
| Scrubbing | Precipitates on probe "scrub" SO ₂ from sample gas. | Blowback. Redesign. | 3-3, 3-4 |
| Probe Problems — Dilution Extractive Systems | | | |
| Pressure Effects | Pressure changes affect dilution ratio causing measurement errors. | Calculate correction. | 3-5, 3-6 |
| Temperature Effects | Temperature changes affect dilution ratio causing measurement errors. | Calculate correction. Add probe heater. Replace with ex-situ probe. | 3-5, 3-6 |
| Droplet Scrubbing | Evaporation of droplets in sonic probe can plug probe or cause pre-diluting and inconsistent measurements. | Attach demister. Replace with ex-situ probe. | 3-5 |
| Multi-Component Cal Gas Effect | Mixtures of cal gases may alter the expected gas velocity through the sonic orifice, biasing measurements. | Calculate correction. Use gas mixtures consistently. | 3-6-3-8 |
| Contaminated Dilution Air | Trace amounts of measured gas in dilution air cause errors. | Check zero baseline with high quality zero air. | 3-9 |
| Varying Dilution Air Pressure | Poor quality dilution air regulator adversely affects dilution ratio. | Install flow controllers or better quality pressure regulators. | 3-9 |
| Other Sampling System Problems - Source-Level Extractive Systems | | | |
| Water Entrainment | Collected liquid can scrub soluble gases, dilute sample gas, or cause leaks through corrosion. | Redesign. | 3-9, 3-10 |
| Leaks | In negative pressure systems, leaks may dilute sample gas. | Find and remove leaks. | 3-10, 3-11 |
| Adsorption | Gas adsorbs on walls of tubing causing measurement errors, particularly at low emissions concentrations. | Increase flow rate. | 3-11, 3-12 |
| Absorption | Gas is absorbed in moisture condensed in the H ₂ O conditioning system. | Remove moisture. Acidify condensate. Change system design. | 3-12, 3-13 |
| Moisture Monitor Errors | Systematic error in moisture monitor may produce bias. | Factor in error from moisture monitoring in test calculations. | 3-13 |

CHAPTER 3

SOURCES OF BIAS IN EXTRACTIVE CEM SYSTEMS

3.1 INTRODUCTION

A number of CEM extractive system designs are available that can be selectively applied to best monitor a plant's emissions. There is no "best" system for all applications, since each type of system will have its advantages and shortcomings in any given application. Extractive systems can be categorized as shown in Table 3-1 (Jahnke, 1993).

Table 3-1. Types of Extractive CEM Systems

| |
|---|
| <p>Source-Level Extractive</p> <ul style="list-style-type: none">⊆ Hot-wet⊆ Cool-dry<ul style="list-style-type: none">– Conditioning at probe– Conditioning at shelter |
| <p>Dilution-Extractive</p> <ul style="list-style-type: none">⊆ In-stack dilution probes⊆ Out-of-stack dilution |

Each type of system will be prone to different types of sampling errors. The types of problems that occur can generally be categorized as follows:

- ⊆ Probe effects
 - Probe filter: Plugging and scrubbing
 - Dilution probe: Temperature (T) and pressure (P), gas density (D) effects, and water droplet evaporation
- ⊆ Water entrainment
- ⊆ Leaks
- ⊆ Adsorption: Wall losses
- ⊆ Absorption: Conditioning systems

These potential sources of sampling error and bias are illustrated in Figure 3-1.

3.2 PROBE EFFECTS

CEM system sample probes used in fully extractive systems usually incorporate an external filter, internal filter, or both, to prevent particulate matter from entering the sample line. Most

systems incorporate a "blowback" cleaning cycle, where high-pressure air is periodically blown back through the filter to remove accumulated materials. In some cases, this procedure may not be effective, especially if particulate matter is sticky or if a particulate cake builds up rapidly due to a process upset. Under these conditions, sampling problems occur.

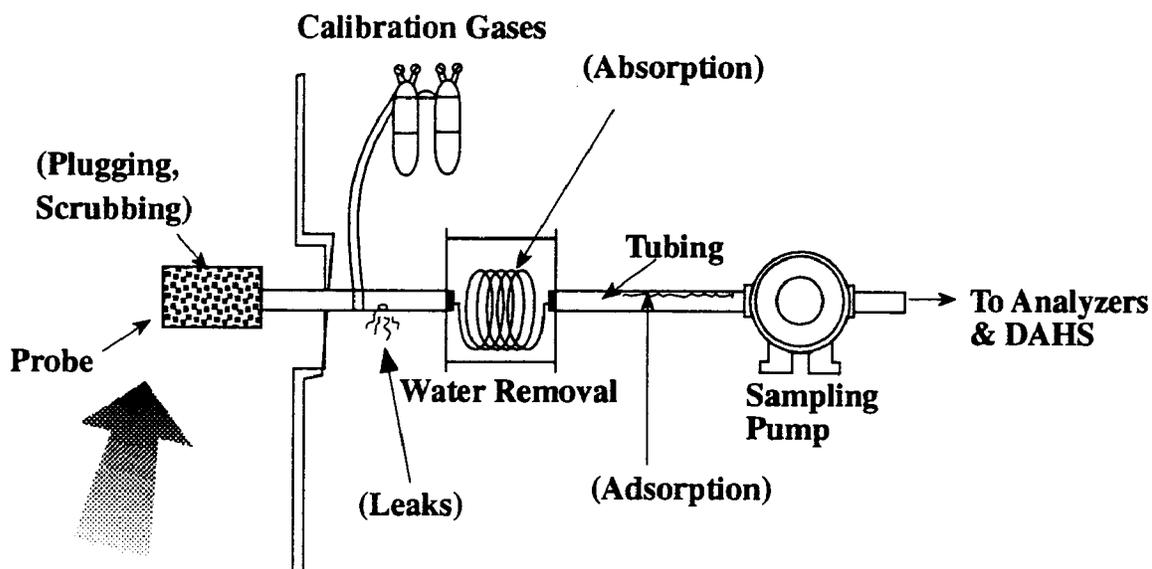


Figure 3-1. Potential Sources of Bias in Extractive Systems

3.2.1 Source-Level Systems

Probe plugging is generally a catastrophic event that calls for corrective action on the part of the instrument technician. However, the occurrence of plugging can give rise to conditions that produce systematic errors even after the plugging itself is corrected. A plugged probe will prevent sample gas from being analyzed, and therefore the emission levels would be seen to decrease. However, the plugging will cause the vacuum in the sampling system to increase. Weaknesses in the system—poorly tightened fittings, cracks in the sampling line, poorly constructed valves, etc., would be strained. A leak may therefore develop and persist after plugging is corrected. The leak will, of course, cause the sampled gas to be diluted and the gas concentration will subsequently read lower.

It is also possible that the probe filter can become only partially plugged and the material adhering to the filter reacts with the gas or gases to be measured. CEM systems installed after wet scrubbers may be subject to scrubber upsets where calcium sulfates, lime, etc., may precipitate on the probe or filter surface. This precipitate may then "scrub" SO_2 from the sample gas before entering the extractive system. This problem can lead to systematically low readings and can be difficult to detect. A probe calibration check should detect this problem if the calibration gas is injected directly ahead of the probe filter. The value obtained will be lower than that obtained by conducting a "local" calibration check at the gas injection port of the instrument.

Blowback systems (Figure 3-2) may be helpful in minimizing scrubbing problems. However, scrubbing loss of SO₂ may be disguised if the blowback cycle takes place before the calibration cycle and not after it. The probe and filter would be relatively clean after the blowback cycle, and the SO₂ concentration would not decrease appreciably. Corrective action involves extracting, disassembling, and cleaning the probe and probe filter immediately after the upset.

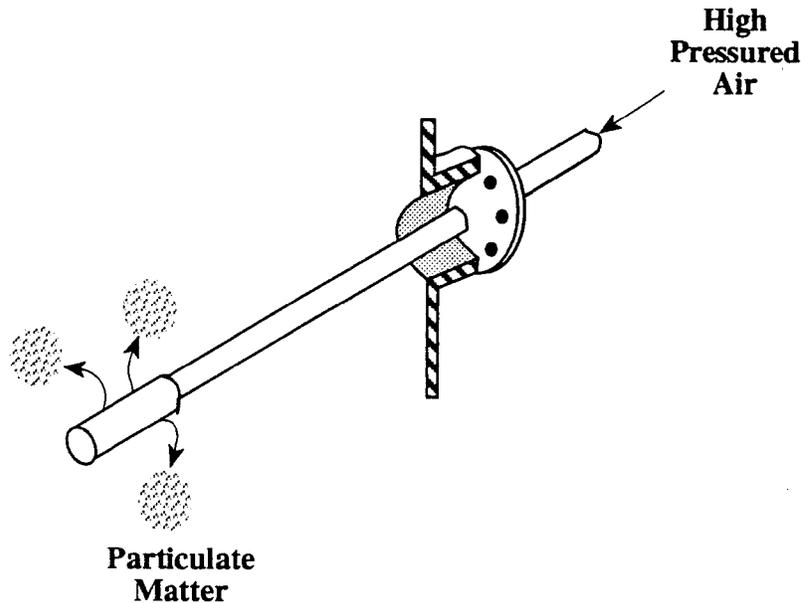


Figure 3-2. Probe Blowback

Scrubber upsets are occasions when monitoring emissions is most important. CEM system downtime and loss of data during this period are significant concerns. The probe calibration system should be designed or redesigned to be unimpaired by any such upsets or scrubbing effects—internal probe filters would be more suitable for this application than external probe filters.

If a probe filter with too great a porosity (i.e., greater than 1–3 Fm) is used, fine particles can enter into the sampling line and then scrub gases by reactive or adsorptive processes (see also discussion below). If the process is adsorptive, it may take a relatively long time for the system to reach an equilibrium calibration value after a zero check, or vice versa. The zero gas would sweep the gas off the particulate matter during the zero check, but the gas would re-adsorb during the span check. If water condenses in the sample line of such a system, the particles may agglomerate to form a mud, which can subsequently plug downstream components. Corrective action must then be taken.

The problem of poorly sized probe filters (in terms of porosity and surface area) should be addressed before certification, since the resulting bias problems cannot be easily corrected. Not correcting this problem before certification is likely to make it necessary to perform more frequent preventive maintenance, such as routine sample line cleanings that are difficult to conduct and subject the system to disassembly/reassembly problems.

3.2.2 Dilution Probes

Dilution probes are widely used in Part 75 CEM systems because dilution systems can directly measure gas concentrations on the wet basis consistent with the flow measurements used to compute SO₂ mass emission rates (see Eq. 2-1). A further advantage of dilution systems results from their ability to draw in flue gas at sampling rates significantly less than source-level systems (20–50 cc/min versus 2–5 L/min). Most particulate matter will continue past the probe, with only gas being drawn into the system. Low flow systems have been applied to many difficult sampling situations, precisely because the need to filter particulate matter is minimized.

However, in wet scrubber applications, aerosol droplets may enter the dilution probe. Evaporation of the droplet in the sonic orifice can cause dissolved solids to precipitate and plug the probe. Also, evaporation of the droplets will increase the volume of water vapor in the sample, pre-diluting it to give inconsistent measurements. It may be possible, in some applications, to remove these droplets by attaching a demister to the dilution probe inlet.

Dilution probes and out-of-stack (or "ex-situ") dilution systems offer many advantages over source-level extractive systems. Because the dilution reduces the moisture content to dewpoints typically in the range of -20EF to -40EF, heated sample lines and chillers are not necessary. Consequently, maintenance requirements are somewhat less in dilution systems than in source-level extractive systems. Dilution probes and the ex-situ systems are, however, more sophisticated devices than they might at first appear to be. Most of these devices incorporate a critical orifice: a glass or sapphire tube, or orifice plate. The performance of critical orifices in CEM applications has not been well understood and has only recently been examined in detail.

Dilution probes are affected by changes in the absolute stack pressure, stack temperature, and the sample gas molecular weight. The dilution ratio can change with a change of any one of these parameters. This observation has led to much confusion in their application and certification, particularly in Part 75 applications where greater system accuracy is desired. For example, if a dilution system is calibrated at a stack absolute pressure, and the calibration is then checked 24 hours later after a change in pressure has occurred, the system response will be different from that obtained previously. Note that the absolute pressure, P_{abs} , is the sum of both the barometric pressure, P_{bar} , and the stack static pressure, P_s , (e.g., $P_{abs} = P_{bar} + P_s$). Therefore, the pressure change from Day 1 to Day 2 could have resulted from a change in the stack pressure due to a change in plant operating conditions or in weather conditions (e.g., a reduction in atmospheric pressure from an incoming storm front). Also, if the stack or duct temperature changes by several hundred degrees, for example during a unit outage, there will be a problem. If a probe calibration is conducted during the outage (lower temperature condition), the dilution probe system will not read correctly when the temperature is brought back up.

For the dilution probe*, the pressure effect has been found to be linear, corresponding to approximately a 1% increase in reading for a 3.45-in. H₂O increase in absolute pressure (Jahnke et al., 1994). The temperature effect appears to be nonlinear, corresponding to approximately 1% increase in reading for a 50EF drop in temperature. These values may be system specific, although a similar pressure dependence has been found for the EPM dilution probe by other investigators.

With the advent of Part 75 CEM system requirements, many dilution probe system vendors are applying corrections for stack pressure and temperature effects. Pressure is monitored either independently or through the dilution probe calibration tube. Stack temperature is monitored using a thermocouple or resistance thermometer. Either theoretical or empirical algorithms incorporated in the CEM computer are used to correct the data to improve data accuracy. The pressure correction factors used are typically in the range of 3.4- to 4-in. H₂O/percent change in reading. When properly applied, such corrections have been found to improve data quality and minimize system drift due to pressure changes.

Correcting for temperature changes has been found to be somewhat more problematic. Due to the apparent nonlinear response to temperature changes, accurate temperature correction factors have been more difficult to obtain. Such factors may be adequate for small swings in temperature (i.e., less than 50EF), but for cycling units or other plants where wide swings in temperature are experienced, the use of correction factors has not always proven satisfactory. One solution is to place a heater around the dilution probe to keep it at constant temperature. Another solution to probe temperature problems is to dilute the flue gas sample outside of the stack (Fischer, 1993). External dilution systems (i.e., the so-called "ex-situ" dilution systems) can be heated relatively easily to maintain a more constant temperature. In addition, the ex-situ systems solve aerosol problems in scrubber applications. The ex-situ probe, when sloping into the stack, allows droplets to condense and run off back into the stack before they reach the critical orifice. The ex-situ systems allow somewhat more flexibility in difficult sampling situations, but pressure corrections are still necessary. The various approaches to correcting for pressure and temperature bias problems in dilution systems are summarized in Figure 3-3.

Dilution systems have also been found to be sensitive to the molecular weight of the sampled gas (Appel, 1994; Miller, 1994). This becomes particularly an issue in system calibration. In the past, it was common practice to calibrate CEM systems with single component gas blends (e.g., SO₂ in nitrogen or in air). With the advent of the Acid Rain Program, there has been increasing interest in using multicomponent protocol gases for the daily calibration error and the quarterly linearity testing. The multicomponent gases offer cost savings by reducing the number of cylinders necessary per system, and they can model emissions closer than single component gases. A common multicomponent blend is the "triple blend" containing SO₂, NO, and CO₂, where the CO₂ concentration may be 20% of the total gas composition.

* The findings discussed here are based on laboratory and field tests of the EPM probe.

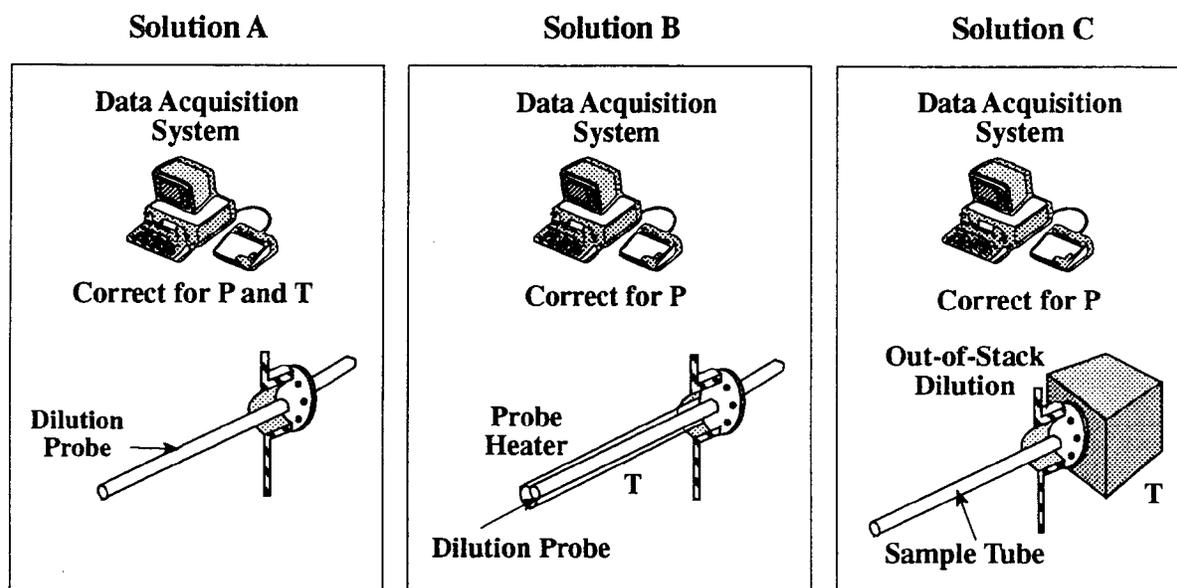


Figure 3-3. Solutions to Dilution System Bias Problems

In a triple blend containing CO_2 , the heavier CO_2 (molecular weight 44) replaces the air (molecular weight 29) or nitrogen (molecular weight 28) that are normally used as make-up gases. The average molecular weight of the triple blend will therefore be different than that of a single-blend gas. Because of the molecular weight dependence of the critical orifice, a dilution system initially calibrated with a gas mixture of 900 ppm SO_2 in nitrogen will not read correctly a 900 ppm SO_2 triple-blend gas containing 20% CO_2 . This has important consequences in system calibration, the actual emission measurements, and quarterly linearity checks. Biases in dilution system response up to 7% have been calculated for different combinations of gas blends and flue gas compositions (McGowan, 1994). Conditions that can result from this effect are summarized in Table 3-2.

Several potential approaches can be used to resolve these issues. The most straightforward one is to use for calibration, calibration error checks, linearity, and RATAs, triple-blend gases containing CO_2 at a concentration close to that contained in the flue gas. However, this solution is problematic when the regulations specify using a CO_2 calibration gas concentration (as, for example, in the linearity check) whose level differs from that normally found in the flue gas. Another solution is to correct empirically the dilution system response for the differences in molecular weight (Appel, 1994). Because the CO_2 concentration of the flue gas is measured and the molecular weights of the calibration gases can be calculated, this calculation can be performed easily. Appel suggests normalizing all data to a nitrogen background value to obtain a consistently accurate system response. Another suggestion (Miller, 1994) recommends the use of "matrix-balanced" multicomponent gas mixtures in which additional lighter gases are included in the multicomponent gas mixtures to offset the higher molecular weight contribution of the CO_2 . These remedies are summarized in Table 3-3.

Table 3-2. Effects of Gas Blends on Dilution System Measurements

| Activity Performed | Calibration Gas Blend Used | Possible Resulting Measurement Biases |
|--|---|--|
| Emissions Measurements | CEM system calibrated with CO ₂ triple blend | Emission measurements bias minimized (because CO ₂ present in both flue gas and calibration gas). |
| | CEM system calibrated with single blend (e.g., SO ₂ in nitrogen) | Emission measurements are biased (because CO ₂ present in flue gas). |
| Calibration Error Test and Linearity Check | CEM system calibrated with single blend | Calibration error test conducted with CO ₂ triple blend will show a bias. Linearity check conducted with CO ₂ triple blends will show bias. |
| | CEM system calibrated with CO ₂ triple blend | Calibration error test conducted with single blend will show a bias. Linearity check conducted with single blends will show bias. |
| RATA | CEM system calibrated with single blend. | RATA conducted with Reference Method 6C calibrated with a CO ₂ triple blend will show bias. |
| | CEM system calibrated with CO ₂ triple blend. | RATA conducted with Reference Method 6C calibrated with a single blend will show bias. |
| | CEM system calibrated with a single blend. | RATA conducted with Reference Method 6C calibrated with a single blend will minimize bias. |
| | CEM system calibrated with CO ₂ triple blend. | RATA conducted with Reference Method 6C calibrated with a CO ₂ triple blend will minimize bias. |

Whichever approach is taken, consistency must be exercised. Auditors or source testers must be notified of the need to maintain consistency with respect to the system being measured and the gases used in its calibration. An auditor's improper choice of calibration gas could lead to the failure of an audit or certification test.

Also, Miller (1994) has noted that calibration gases certified using luminescence analyzers may be subject to "quenching" effects due to the percent level CO₂ present in the triple blends (Miller, 1994). Today's analyzers have been designed to minimize this effect (Appel, 1994), but it may be necessary to investigate this issue further if molecular weight corrections do not account for discrepancies observed. The remedy here is simple: only multicomponent blends that have been certified using an instrument unaffected by quenching or that have been corrected for quenching effects should be used.

Table 3-3. Remedies to Molecular Weight Effects in Dilution System Response

| | |
|---|---|
| C | Use CO ₂ multiblends consistently for daily calibration, calibration error checks, linearity checks, and RATAs. |
| C | Determine source-level and calibration gas molecular weights and normalize or otherwise correct CEM system response through the DAHS. |

The performance of dilution probes is extremely dependent upon the quality of the dilution air. Most dilution systems use air clean-up systems that remove trace amounts of water, CO₂, CO, and other contaminants in the pressurized gas. If even trace amounts of one of the measured CEM system gases is present in the dilution air, a response will be seen on the ambient air analyzers used in these systems. Since dilution ratios of 50:1 to 300:1 are common, contaminated dilution air can easily cause the monitoring instruments to go off scale. Normally, either plant instrument air is used for the dilution, or a dedicated compressor may be installed specifically for the system. In case the air compressor or the air clean-up system fails, cylinders of high-grade zero air can be used as an interim measure. In any event, good quality control practice should specify that high-quality zero air be used to periodically check the zero baseline values of the CEM system, particularly if the dilution air is also used for the daily calibration error checks.

Another problem occurs in dilution systems when the dilution air pressure varies. In poorly regulated systems, fluctuations in the plant instrument air pressure can be reflected in this supply and can affect the dilution ratio. In particular, if the gas flow through the orifice becomes subsonic, the dilution ratio will no longer be constant. Such problems often become evident during the seven-day calibration error test: the system appears to drift for no apparent reason. Mass flow controllers or high-quality pressure regulators installed into the dilution air control system can alleviate the condition.

3.3 WATER ENTRAINMENT

Water entrainment into a source level hot-wet system or dilution systems can bias the data low. If water droplets enter the probe and then evaporate, their relatively larger volume as vapor will reduce the pollutant gas concentration. A heater used to vaporize the droplets before they enter the probe or a filter may be counter-productive, since the vaporized droplets would then also be volumetrically diluting the sample.

If water droplets enter the probe and do not evaporate, soluble gases can be absorbed in the droplets and scrubbed from the sample gas stream. Also, if the sampling system is not adequately heated (including the probe, umbilical line, valves, and regulators in contact with the hot flue gas), water or acid can condense. This condensed liquid can again scrub soluble gases.

Water droplets or condensed liquid are also likely to corrode the system at the point of contact and cause a leak to develop. Even worse, if particulate matter has entered the system, the liquid can produce a mud that plugs up the system.

3.4 LEAKS

Leaks in the sampling system may dilute the sample gas. In negative pressure regions of an extractive system, air leaking into the system will dilute the sample and possibly cool it and condense water into the sample line before it reaches the condenser. For constant leak rates, this will give a constant, low bias due to the dilution. Condensed water may also scrub gases from the sample stream before they reach the analyzers.

Positive pressure systems are less prone to leak biases than are negative pressure systems. In these systems, gas is "pushed" through the sample line into the analyzer manifold or analyzer. Here, a positive pressure is exerted on the line; if a leak is present, sample gas will leak out, as opposed to air leaking in. Dilution systems, as well as some source-level systems, are positive pressure systems. In a source-level system, however, the pump may be placed before the moisture removal system and, unless heated, may be more maintenance prone than if it were located after the condenser.

Leaks in calibration gas lines can also be a problem. A bias would be introduced in calibration if the gas is diluted before it enters the analyzer. Also, depending on the system configuration, air could dilute the sample gas through the calibration gas line when in the sampling mode.

Although difficult to detect and locate, leaks can be found when conducting a calibration error check. It is important, however, for the sample stream pressure and flow rate to be the same during the check as during normal sampling. If a probe calibration check is conducted in a negative pressure system, the calibration gas should be vented to the atmosphere so that the pressurized calibration gas is not "pushed" through the sampling system. This external atmospheric vent audit technique (Reynolds, 1989) exhausts excess gas through a rotameter to the atmosphere as the CEM system pump pulls in the injected gas. In this procedure, the data must be considered carefully. Lower instrument readings can easily be misinterpreted as not being due to leaks, but as being caused by electronic problems, instrument drift, or bad calibration gas. The effect of the leak may then be adjusted out incorrectly as analyzer drift.

For source-level systems, the best way of checking the sample system integrity is to first calibrate at the instruments, not through the probe. Since the sampling system is by-passed, the analyzer should read properly both the zero and the calibration values. Then, conduct a probe calibration. If the calibration value is decreased, sample losses due to leaks, absorption, or adsorption may be present. Alternatively, if a calibration gas that has nitrogen as the make-up gas instead of air is injected at the probe, any response on an oxygen analyzer will indicate a leak.

Another method of checking for leaks is to pressurize the system with air or nitrogen and wipe suspected fittings or valves with a soap solution. Bubble formation indicates the presence of a leak. Another method is to inject helium or a tracer gas such as carbon tetrachloride into the system and use a hand-held leak detector for determining the presence of any released material.

Leaks are corrected by first checking the ferrules of the fittings and then either (a) tightening system fittings; (b) replacing leaking, corroded parts; (c) replacing poor-quality valves and other components with higher-quality components less likely to leak; or (d) redesigning and simplifying the system so that there will be fewer components likely to leak. Leaks may produce a constant bias that could be adjusted out either electronically or through the data acquisition system if a constant leak rate is known. However, this approach is bad practice and is not commonly done. The leak could worsen or could in fact be variable (dependent on ambient temperatures, pressures, sampling rates, etc.). The best solution is to find the leak and fix it.

3.5 GAS ADSORPTION

Bias effects due to gas adsorption on the walls of gas tubing or internal instrument cell surfaces are generally noticed when checking a system with dry calibration gases. A system may need to be "passivated" or "conditioned" prior to use. Dry zero gas may destroy this passivation, which may result in the system taking an inordinate length of time to reach the span gas value when undergoing a calibration check. These effects are particularly noticeable at very low concentrations (i.e., less than 10 ppm) and with certain types of analyzers. Since adsorption effects lead to biases on the order of a few ppm, they become more noticeable at the lower concentrations where they can lead to significant measurement inaccuracies. It can be pronounced in dilution systems at low ambient temperatures, when the sample line is not heated or freeze protected. Adsorption does not affect the steady-state concentration measured at the analyzer but may result in long response times (McNulty et al., 1974). Bias may result if the operator is not aware of this effect, particularly if the operator or computer does not wait for the system to come to an equilibrium condition.

McNulty et al. (1974) conducted an adsorption study using 15.2-m lengths of different sample line materials. Tests were conducted using 1200 ppm levels of SO₂ and NO. The fall time results are given in Figure 3-4, where the desorption from the walls results in greater tailing and greater response times. O₂, CO₂, and CO do not commonly adsorb on most sample line materials. NO, SO₂, and NO₂ show increasing adsorptive properties, respectively.

The problem may be minimized by (a) adopting a consistent calibration procedure accounting for adsorption effects, (b) sampling at higher gas flow rates, (c) reducing the length of sample lines, (d) heating the sample line, (e) redesigning the analyzer using a sample cell with nonadsorptive surfaces, or (f) replacing the system/analyzer with one in which the effect is less pronounced or non-existent (e.g., in-situ monitors).

Adsorption is also a function of the condition, age, or abuse of the extractive system components. Corroded surfaces, particulate deposits, or condensed organic materials all lead to greater adsorption. It is therefore important to ensure that the sample gas does not condense in the line and to ensure that the condensate in dry extractive systems does not break through and enter the analyzers.

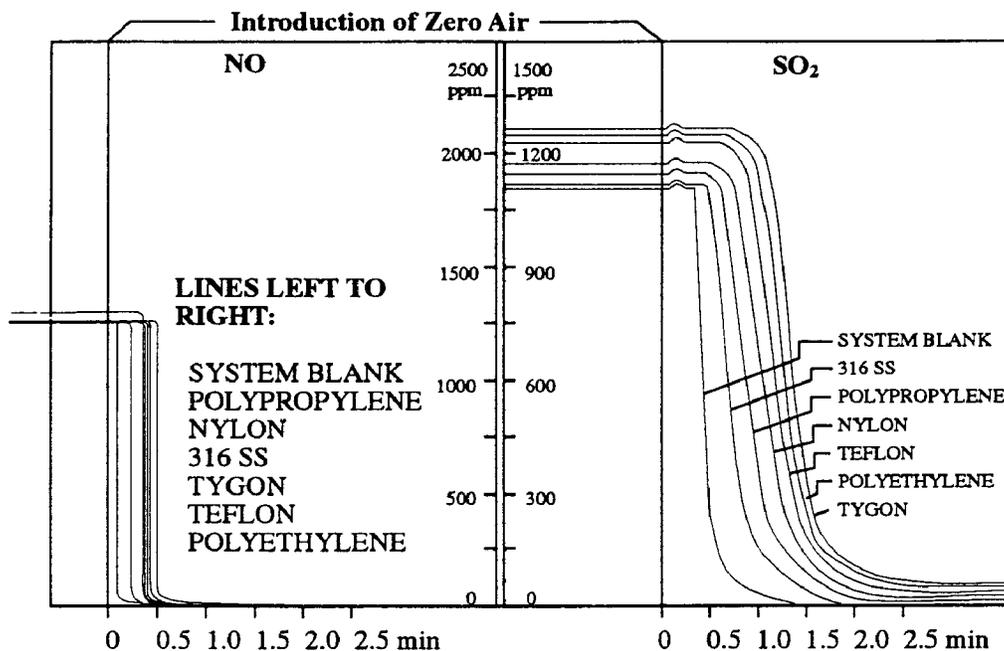


Figure 3-4. Desorption Times of NO and SO₂ with Various Clean Sample Line Materials at a Length of 15.2 m (McNulty, 1974)

3.6 ABSORPTION

Soluble gases may be absorbed in moisture condensed in conditioning systems designed to deliver a dry gas stream to the analyzer. Poorly designed systems may allow too great a contact time between the dried gas stream and the collected liquid, or the soluble gas may be absorbed upon condensation of the moisture. This effect is more noticeable at the lower pollutant gas concentrations (i.e., less than 100 ppm) but becomes smaller as the collected liquid increases in acidity.

Freitag (1993) found that for SO₂ at concentrations on the order of 100–1,000 ppm that, under a variety of conditions, from 3–15% of the SO₂ could be lost in the chiller. The work also projects that at SO₂ levels of 10 ppm at 20% moisture, losses can be on the order of 30%. Freitag's general observations follow:

"The fraction of SO₂ removed from the analysis by a refrigerated trap:

- (1) increases with increasing moisture content of the stack gas,
- (2) increases with decreasing SO₂ content, and
- (3) increases with decreasing trap temperature."

These losses can be calculated if the stack gas dewpoint, sample gas flow rate, wet basis SO₂ level, SO₂ solubility, and condenser temperature are known.

Gas absorption may be reduced by (a) continuously removing collected liquid from the conditioning system (a practice that is almost mandatory for the proper operation of chiller systems), (b) acidifying the condensate to reduce SO₂ solubility, (c) acidifying the gas stream with an unmonitored acid to reduce SO₂ solubility (DeFriez, 1992), and (d) using some other method of moisture removal such as Nafion™ driers (Kertzman, 1973).

Alternatively, another type of CEM system that does not condense flue gas moisture, might be selected. Hot-wet source-level systems avoid the problem. In-situ monitors and dilution systems will also not incur solubility losses; however, these methods may have difficulty measuring at the lower concentration levels (less than 10 ppm) where the losses are most pronounced.

3.7 DRY EXTRACTIVE SYSTEMS AND MOISTURE MEASUREMENTS

The use of dry extractive systems in Part 75 Acid Rain Program applications requires the measurement of flue gas moisture content. Because of the form of Eq. 2-1 used to calculate emission rates of lbs/hr, the SO₂ gas concentration must be determined on a wet basis to be consistent with the wet basis volumetric flow measurement. In dry extractive systems that use a chiller, water is removed from the sample gas and gas measurements are made on a dry basis. Some means of determining the flue gas moisture content must therefore be incorporated into the CEM system.

In some Part 60 CEM applications, flue gas moisture contents have been assumed or given a constant value based on stack test measurements. In other cases, saturation is assumed and the moisture content is determined by monitoring the flue gas temperature. Assuming a constant value is not, in general, appropriate to Part 75 systems unless the moisture content is constant enough to meet Part 75 system performance requirements. A number of moisture monitors are available on the commercial market. However, methods of calibration for these devices are rudimentary, and no standards have been developed for their performance. A typical technique has been to measure O₂ on both a wet and dry basis and then to calculate the moisture content from a ratio of the measurements. In this technique, the calibration of the O₂ analyzers can be checked with reference gases. The introduction of moisture analyzers into a CEM system therefore introduces another source of measurement error that must be accounted for in calibration error, linearity, relative accuracy, and bias tests.

3.8 SUMMARY

A number of problems can occur in extractive systems. Some of the problems produce relatively unvarying systematic error and may therefore be addressed by a one-time or periodic physical adjustment or calculation "fix." However, even though a problem may be amenable to a corrective calculation, it is preferable to eliminate the source of the error, rather than make "corrections" for it. Other problems produce varying systematic error that may be either episodic, increasing, or decaying. Such problems are not amenable to calculation corrections. It is then best to either correct the problem or redesign the system so that the problem will not reoccur. Recommended action for the problems discussed above are summarized in the table on page 3-1.

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CHAPTER 4

SOURCES OF BIAS IN IN-SITU MONITORING SYSTEMS

Chapter 4 Highlights

Sampling System Problems — In-Situ Gas CEMS and Opacity Monitors

| Problem | | Corrective Actions | Page Refs |
|--|---|---|--------------|
| Name | Description | | |
| Point Monitors | | | |
| Blinding | Precipitate on the filter seals the probe tip from the flue gas. | Clean or replace filter. | 4-4 |
| Faulty Audit Gas Injection | Improper flow rate of calibration gases results in biased concentrations in probe cavity. | Adjust flow, carefully following calibration procedures. | 4-4 |
| Temperature Distortions | If temperature sensors are not working properly, errors can result in emission values. | Calculate correction. Adjust or replace sensor. | 4-5 |
| Path Monitors | | | |
| Internal Calibration Cell Defects | Errors are introduced when internal calibration cell leaks or its gas decomposes. | Check daily cal chart for jumps or drift. Replace cell. | 4-5-4-7 |
| Gas Cell Temperature Problem | Bias results if the temperature of the gas cell and flue gas differ greatly. | Correct mathematically. Install cell in "zero pipe" or outside stack in heated area. | 4-9 |
| Flow-Through Calibration Gas Availability | Protocol 1 gases often not available at required concentrations. | Use only if certified gases are available. Redesign system - use longer cell. | 4-7-4-10 |
| Transmissometers (Opacity Monitors) | | | |
| Improper System Design | Poor design produces both bias and inconsistencies with visual observations. | Redesign. | 4-10 |
| Dirty Windows | Build-up on windows produces bias. | Auto-correct. | 4-10 |
| Interferences | Water droplets and high NO ₂ distort measurements. | Calculate correction. | 4-10 |

CHAPTER 4

SOURCES OF BIAS IN IN-SITU MONITORING SYSTEMS

4.1 INTRODUCTION

In-situ systems are used to monitor pollutant gases, O₂, CO₂, flue gas velocity, and flue gas opacity. These instruments monitor the flue gas "in-situ," in the stack without extraction. In-situ gas monitors were developed in response to maintenance difficulties and availability problems associated with source-level extractive systems. However, in-situ monitoring does not relieve the user of monitoring problems. Different types of measurement errors and biases can occur, such as those associated with flue gas stratification (discussed in Chapter 2).

In-situ monitors can be classified into two basic categories, point and path. Point monitors measure at a single point in the stack (strictly speaking, a short path generally 5–10 cm in length). Path monitors measure from one side of the stack or duct to the other. There are several options within these two categories, as listed in Table 4-1.

Table 4-1. Types of In-Situ CEM Systems

| Pollutant/Diluent Gases | Velocity (Volumetric Flow) | Opacity |
|------------------------------------|---|------------------------------------|
| Point | Point Single point Multiple probe Averaging probe Probe arrays | |
| Path Single Pass Double Pass | Path Two pass Multi-pass | Path Single pass Double pass |

Path monitors can be of either single-pass or double-pass design. Single-pass gas concentration monitors typically project a beam of light across the stack to a detector. Single-pass systems, once popular for gas monitoring in the 1970s, are no longer widely marketed due to difficulties associated with their calibration. The double-pass systems return the light beam from the opposite side of the stack back to a detector in the transceiver assembly, which also houses the projection lamp. Double-pass systems can be calibrated by a number of techniques and a new generation of these systems is being applied to a variety of sources.

A variety of point and path methods have been developed for monitoring flue gas velocity, the different approaches representing attempts to overcome problems associated with velocity stratification. In cases of uniform, fully developed flow, the simplest approach is to measure at one or two points in the stack. If the flow pattern changes frequently, multiple probes or averaging probes can be applied. In the worst cases, an array of sensors can be installed to monitor at Reference Method 1 traverse points. The ultrasonic path monitors use two transducers to pass sound pulses with the flow and against the flow. In multi-pass systems, more than two transducers can be used to grid the cross-section further.

One of the major problems associated with gas path monitoring systems and all velocity monitoring systems is that methods for **independently** checking system calibration are limited. In contrast to extractive and point in-situ gas monitoring systems, where independently certified gas can be easily routed into the system, path monitors for measuring gases must add special flow-through calibration cells. Velocity monitors all use internal calibration methods that are not referenced to independent, certified standards. These instruments may use a "reference" sound pulse, a "reference" voltage, or a "reference" pressure, but these "references" are generated by the instrument and in most cases are only electrical checks and do not check the sensing element itself. Ultimately, the only completely independent method for detecting bias in these systems is performing a RATA.

4.2 BIAS IN IN-SITU POLLUTANT AND DILUENT GAS MONITORS

4.2.1 Point Monitors

Point in-situ gas monitors are subject to a number of specific problems and biases. These problems tend to be unique to the measurement method, but several general observations can be made. First, consider a typical in-situ point monitor as shown in Figure 4-1.

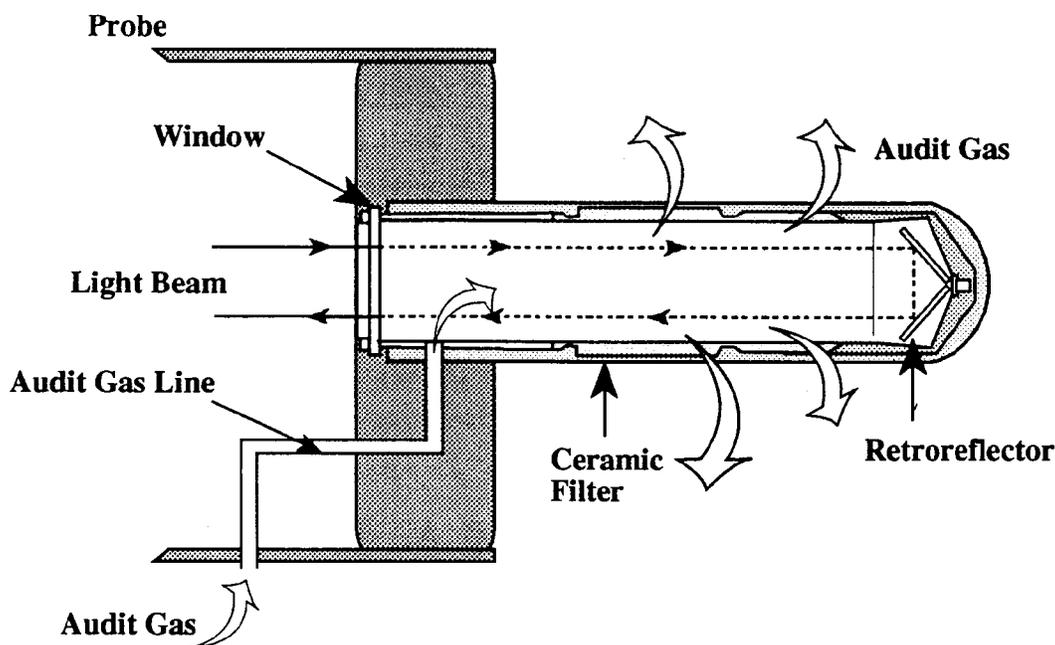


Figure 4-1. A Typical In-Situ Point Monitor for Measuring Gas Concentration

A typical system consists of a measurement cavity that incorporates a gas sensor or a cavity in which light absorption can take place. A ceramic filter prevents particulate matter from entering the cavity, and a deflection bar limits impaction of particulate matter directly onto the filter to minimize plugging of the filter pores. A gas injection port allows calibration gas to enter the cavity, and, when at a pressure greater than the absolute stack pressure, flushes the flue gas out of the cavity. At an "appropriate" pressure, the calibration of the system can be checked.

There are several generic problems that can arise in these systems:

Stratification. Since the monitor is sampling at a point, gas stratification can result in a misrepresentation of the total flue gas concentration, as discussed in Chapter 2. Although measurements can be conducted at a "representative" point, that point must be consistently representative through changing plant operating conditions. It is sometimes difficult to obtain a probe of a length that will position the sensor at a representative measurement point. In-situ probes come in standard lengths and a probe might have to be customized for the application. Structural factors limit probe length; if the probe is too long, it may sag or oscillate in the moving gas stream, either of which can lead to catastrophic failure.

Blinding. In dirty gas streams, particulate matter can impact on the ceramic filter and plug the filter pores. For systems installed after wet scrubbers, a scrubber upset may cause scrubber liquor to become entrained in the flue gas. The dissolved solids may then precipitate on the filter and in the filter pores, essentially sealing the probe tip from the flue gas. This problem will generally be recognized when a greatly increased period of time is necessary for the monitor to read the flue gas concentrations after a zero or upscale gas injection. The response time of the instrument is, of course, greatly increased.

Audit Gas Injection. Although flue gas can be flushed out of the measurement cavity, if the calibration gas flow rate is too high, the gas in the cavity will be pressurized. This pressurization will lead to a higher calibration gas concentration reading than true and a bias in the system if it is recalibrated based on that value. Conversely, if the flow rate of the zero gas or calibration gas is too low, all of the flue gas will not be flushed from the probe cavity and a bias will again result. If the audit gas flows in too fast, it also may not come up to the stack temperature by the time it is being sensed by the monitoring system, causing another error. These biases can be minimized by following calibration procedures carefully. Reynolds (1989) gives detailed methods for conducting such calibrations.

Temperature Measurement. In-situ measurements are made at stack temperature. Because of this, a thermocouple or resistance thermometer is normally incorporated in the system so that the gas density variations can be accounted for in the concentration measurements. In some cases, temperature measurements are necessary to correct for temperature-dependent spectral absorption characteristics. The nature of these corrections is dependent on the measurement technique, where errors in these corrections may have a substantial impact on measurement bias.

The temperature sensor should be checked periodically; however, because the temperature corrections are performed using absolute temperatures, small inaccuracies may not contribute significantly to measurement error. For large variations in temperature, particularly between unit shut-down and operation, significant measurement problems may occur if the system is calibrated initially at lower temperatures. For optimum performance, in-situ monitor calibration checks and calibration adjustments should always be conducted at operating temperatures.

4.2.2 Line Averaged Measurements

Path in-situ gas monitors perform a line average measurement. Although this type of measurement may give a better correspondence to the three-point average of the reference method, there is no guarantee that the line average concentration is representative of the cross-section area average. In circular stacks, if a line average is used to represent an area-averaged concentration, the gas concentrations near the center of the stack will weight the average unrepresentatively—they will bias the result.

When the gas concentration or velocity profile is stratified, bias can be corrected, as discussed in Chapter 2, by determining the profiles and establishing proper weighting factors or by developing an algorithm based upon the measurement line and the profile. Again, mathematical corrections of this kind are dependent upon the stability of the profiles under different plant operating conditions.

It should be noted that a frequent claim for path in-situ systems is that because more points are measured, the data are more representative; an averaged value is obtained and therefore the results are more accurate. This may or may not be true—the only way to test the validity of such claims is to perform a stratification study and evaluate the profiles with respect to the proposed measurement path.

4.2.3 Internal Calibration Techniques

A new generation of double-pass in-situ gas monitors avoids calibration problems associated with single-pass units. In these new systems, a measuring light beam is returned from the opposite side of the stack using a retroreflector, so that the transceiver assembly will house the "active" optical and electronic components such as the lamp, detector, and spectral filters. A system

calibration is normally performed by moving a mirror, inside the transceiver, into the path of the light beam so that the light does not enter the stack but reflects directly back to the detector. This procedure should give a "pseudo-zero" value that can check the performance of the transceiver assembly. Although the pseudo-zero value may not correspond exactly to a "true" stack zero measurement, it can be correlated with it. This method has been accepted for many years in transmissometer systems and is equally valid in gas monitoring path systems.

To obtain an upscale calibration value, a gas cell containing a known amount of the measured gas or an optical filter can be moved into the light path when the zero mirror is in place. Absorption of light energy by the pollutant molecules in the calibration cell causes the light intensity to decrease at the detector and gives a corresponding upscale calibration reading (Figure 4-2).

As discussed in the next section, such internal gas calibration cells do not meet Part 75 criteria for daily calibration checks because the cell gases are not Protocol 1 gases and usually have concentrations higher than those specified by Part 75. Nevertheless, they are essential for keeping these systems "in tune."

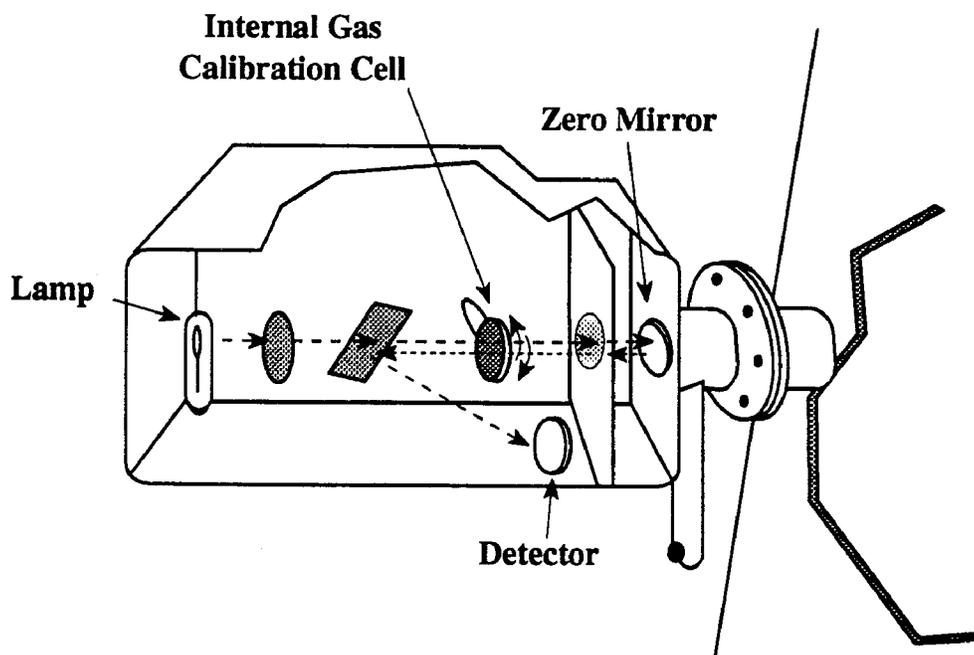


Figure 4-2. An Internal Gas Calibration Cell in a Path In-Situ Monitor

Biases can occur in this calibration method if the internal calibration cell leaks or if the gas inside the cell decomposes. In such situations, calibration adjustment would then be made based on a faulty internal standard and the data would not be representative. These problems can be identified from a calibration QC chart on which the daily calibration responses are tracked. A noticeable jump in drift values or continuously increasing drift values may indicate changes in the calibration cell gas concentration. More commonly, however, RATAs give the first indication that a problem has developed. A failed RATA tends to bring immediate attention to the problem.

Sealed gas cells are made by the instrument manufacturer, but there are currently no third parties that independently certify gas cell concentrations. Although the cells can be checked relatively easily in a spectroscopic laboratory, no programs or protocols have been established to provide certified cell concentration values. This dependence on the instrument manufacturer's values prevents the gas cell calibration technique from being a truly independent audit method.

One single-pass unit performs internal calibration checks using reference spectra. This technique is effective, but even further removed from being an independent check than are the sealed gas cells used in other systems. It is a numerical check based on data stored in the computer memory and does not rely directly on the installed system to perform a reference measurement.

4.2.4 Flow-Through Gas Cell Calibration Techniques

Despite the relative convenience of using internal calibration techniques in path monitoring systems, these methods do not meet performance specification and audit requirements of the U.S. Federal government. In fact, it is specifically stated in Part 75 (U.S. EPA, 1993):

"Design and equip each pollutant concentration and CO₂ or O₂ monitor with a calibration gas injection port that allows a check of the entire measurement system when calibration gases are introduced.....For in-situ type monitors, the calibration must check against the injected gas for the performance of all active electronic and optical components (e.g., transmitter, receiver, analyzer)."

Because of this requirement, flow-through gas cells are now being incorporated into path monitoring systems (Figure 4-3).

The use of flow-through gas cells does provide a valid means of independently checking the monitor performance. However, in current practice, the cells constitute merely an "add-on," applied to satisfy the EPA requirements for cylinder gas audits and calibration error tests. In most instruments of this type, the actual calibration checks are still conducted using the internal filters, sealed gas cells, or reference spectra. The flow-through gas cell is an extra check that is not integral to the instrument operation. This is in contrast to the use of calibration gases in extractive system analyzers (Chapter 6), where the instruments **are** referenced to the zero and calibration gases.

Several additional problems surface in the use of flow-through gas cells in path in-situ systems. If the gas cell is relatively short with respect to the stack diameter (the measurement path), a high concentration calibration gas must be used. For a cell length on the order of a few centimeters, the gas flowed through the cell may have to be at percent level concentrations to elicit a response.

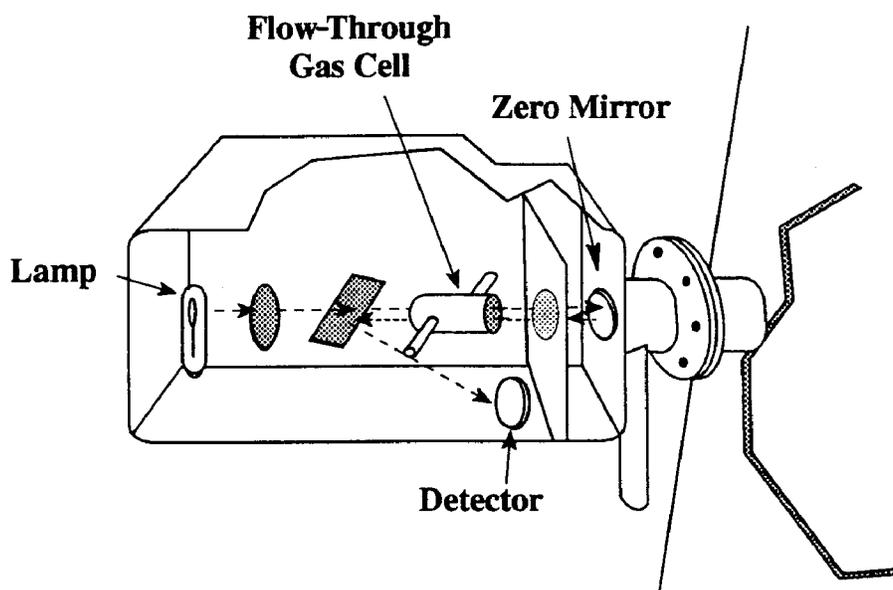


Figure 4-3. Flow-Through Gas Cell for Path In-Situ Monitor Certified Gas Calibrations

This necessity can be seen by considering the "optical depth" of both the stack and the flow-through cell. For path-integrated concentration measurements, the optical depth is defined as the product of the gas concentration, c_s , and the measurement path, d_m , or:

$$\text{Optical Depth} = c_s \times d_m$$

where the measurement path is the distance that the light beam traverses through the flue gas.

Consider, then, if a double-pass path monitor is installed on a 5-m diameter stack having an SO_2 concentration of 1000 ppm, the optical depth will be $2 \times 1000 \times 5 = 10,000$ ppm-m. If the transceiver of the monitor is installed with a 5-cm long flow-through gas cell and the zero mirror is put into place, an SO_2 concentration of 10% would be required in the cell to obtain a cell optical depth of 10,000 ppm-m:

$$\text{Stack Optical Depth} = \text{Cell Optical Depth}$$

$$10,000 \text{ ppm}\cdot\text{m} = c_s \times 2 \times 0.05 \text{ m}$$

$$c_s = \frac{10,000}{0.1} = 100,000 \text{ ppm} = 10\%$$

Conceptually, to reduce the light attenuation by molecular absorption, the number of molecules seen across the stack must be "squeezed" into the cell to obtain a similar instrument response. Required audit and calibration gases would therefore also be at percent level concentrations.

In the CEM quality assurance requirements of Appendix F to 40 CFR 60 and the calibration error requirements of Appendices A and B to 40 CFR 75, cylinder gases traceable to the U.S. National Institute of Standards and Technology (NIST) are required. Specifically "Protocol 1" gases must be used. A problem exists in that Protocol 1 gases at these percent level concentrations are not available. Using other gases not referenced to a national standard is not allowed under the regulations, because it would cause uncertainty in the audit measurement. However, new protocols have been prepared that address this issue (Mitchell, 1993). Note also that since the instruments perform their own internal calibration checks, an incorrect audit gas may not necessarily introduce bias into the system. The instrument could still read correctly, but then might not meet the calibration or audit specifications. Bias would, however, be introduced if adjustments were made with respect to the incorrect gas concentration.

Another issue associated with flow-through cells is that of temperature. The spectral absorption properties of molecules are dependent upon temperature. Therefore, if the flow-through gas cell temperature is appreciably different from the flue gas temperature, a bias in the measurement will be introduced. This bias can be corrected mathematically if the flue gas temperature is measured, and normally constitutes an element of the monitor's programming, where applicable.

Calibration gas problems in path monitoring systems can also be resolved by installing a "zero-pipe" across the stack (Figure 4-4).

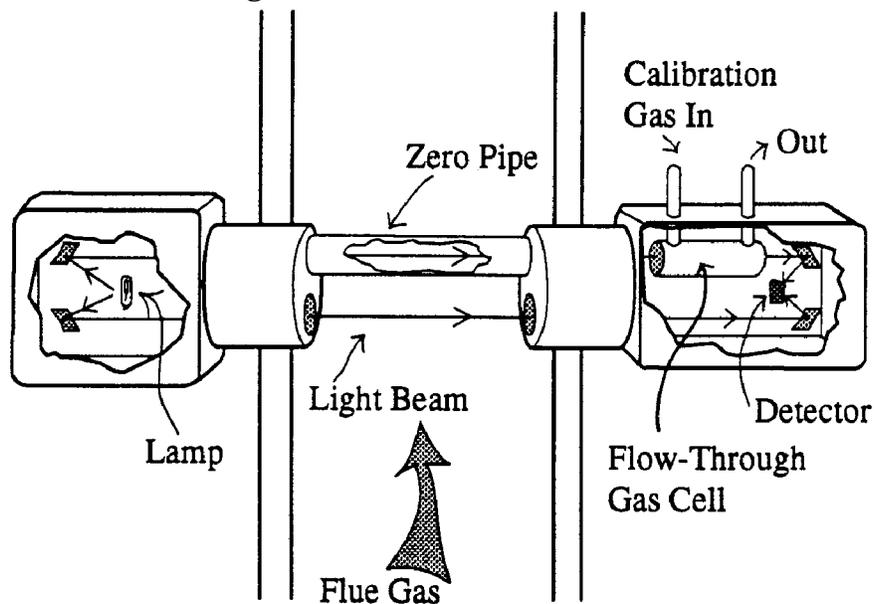


Figure 4-4. Zero-Pipe Configuration

In this technique, the pipe provides an optical path that can be made free of stack gas. The pipe is flushed with clean air when it is desired to check the zero and calibration of the system. A flow-through calibration cell can be incorporated in the pipe so that the calibration gas will be at stack temperature, or the cell can be installed outside of the stack and heated.

The design allows the length of the cell to be adjusted, to meet calibration gas concentration limitations. Calibration gas is normally not flushed through the zero-pipe itself because of the excessive gas volumes required. There are limitations in using this technique because the installation may be difficult, long pipes may sag, and corrosion may be a problem in wet, acidic environments.

4.3 BIAS IN TRANSMISSOMETERS

Transmissometers (opacity monitors) measure the flue gas parameter, opacity. It is intended in U.S. regulations that the flue gas opacity be related to opacity as observed by visual emissions (VE) observers, through the application of Reference Method 9. This requirement has placed design specifications as well as performance specifications on opacity monitoring instruments. Poorly designed opacity monitors, faulty installations, improper calibration, and faulty maintenance can result in inaccurate opacity monitoring data that do not correspond to VE observations.

A thorough discussion of bias in transmissometers is well documented elsewhere (Jahnke, 1984; Plaisance and Peeler, 1988). The reader should refer to these documents to enhance QA plans for opacity monitoring programs.

Briefly, bias can enter opacity measurements by way of the following:

- ⊆ Improper System Design
 - Incorrect spectral response
 - Angle of projection greater than 3E
 - Angle of view greater than 3E
 - Nonuniform beam cross-sectional intensity
- ⊆ Dirty Windows (uncorrected)
- ⊆ Improper Installation - Particulate stratification
- ⊆ Interference by Water Droplets
Possible Interference by High NO₂ Concentrations (Lindau, 1991)

Most of these problems are adequately addressed in modern transmissometer systems. In fact, transmissometers are the most developed of the CEM system instrumentation, commonly having availabilities greater than 98%.

4.4 SUMMARY

Errors of measurement specific to the different types of in-situ monitoring systems are summarized in the table on page 4-1. Systematic errors that can be corrected by calculations or adjustments are identified. Generic sources of bias such as location and stratification and

stack area calculations have not been included in the table, but have been discussed in detail in the text.

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4.6 ADDITIONAL READING

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CHAPTER 5

SOURCES OF BIAS IN FLOW MONITORING SYSTEMS

Chapter 5 Highlights

Flow (Velocity) Monitoring System Problems

| Problem | | Corrective Actions | Page Refs |
|---|--|--|-----------|
| Name | Description | | |
| General | | | |
| Stack Area Miscalculation | Use of incorrect cross-sectional area in calculating volumetric flow can produce measurement error. | Directly measure and re-calculate. | 5-2 |
| Gas Density and Temperature Distortions | Bias can be introduced if the temperature profile is different from the velocity profile. | Verify temperature profile and use new assumptions if there is a disparity with velocity profile. | 5-2 |
| Differential Pressure Sensing Monitors | | | |
| Improper Angle of Probe Tube to Gas Flow | Measurement error can result if probe tube is not oriented perpendicular to flue gas flow. | Rectify improper orientation. Avoid using where cyclonic flow is present. | 5-3 |
| Plugging | Probe plugging can prevent accurate pressure measurements. | Increase frequency and/or pressure of blowback. | 5-3, 5-4 |
| Thermal Sensing Monitors | | | |
| Particulate Build-Up on Sensors | Particulate build-up can slow instrument response by forming an insulating layer on the probe's temperature sensors. | Remove by flash heating or blowing off deposits. Avoid by employing aerodynamic cavity design. | 5-4, 5-5 |
| Water Droplets and Acid Corrosion | Heat lost to evaporation can bias measurements. Acid droplets can eat into the metal junctions of probe arrays. | Repair and change probe design. | 5-4 |
| Ultrasonic Monitors | | | |
| Improper angle of transducers | Measurement errors can result under pitched or cyclonic flow conditions. | Orient measurement path perpendicular to the flow pitch. Where pitched flow is variable, consider using two sets of transducers in X-pattern. | 5-5, 5-6 |
| Particulate build-up on sensors. | Build-up on sensors can introduce measurement error. | Use blowers to keep transducer sensors clean. | 5-6 |

CHAPTER 5

SOURCES OF BIAS IN FLOW MONITORING SYSTEMS

5.1 INTRODUCTION

The major bias problems associated with flow monitoring systems are attributable to velocity stratification in the duct or stack. This issue has been discussed in Chapter 2, but will be amplified here with respect to specific instrumentation.

There are other sources of bias in volumetric flow monitoring systems. From Eq. 2-1, it is obvious that the measurement cross-sectional area is included in the pollutant mass rate expression. Stack and duct cross-sectional measurements obtained from old blueprints or out-dated drawings can introduce biases of from 1% to 2% into the volumetric flow/pollutant mass rate measurement (Traina, 1992). Warping or settled fly ash in horizontal ducts can lead to further errors. This bias will, however, not become evident if the same incorrect dimensions are used in both the CEM system and the source tester RATA calculations. Cross-sectional dimensions should therefore not be assumed, but measured directly. These dimensions can be obtained by measuring the outside circumference of the stack and accounting for the depth of the stack walls and insulation, or more directly, by making surveyor transit measurements through the ports.

Differential pressure and thermal sensing systems must also determine the gas density in order to calculate the flue gas velocity. Gas density is obtained by measuring the flue gas molecular weight, temperature, and pressure. However, most systems monitor the flue gas temperature only and assume values for the molecular weight and pressure. Temperature is relatively easy to measure and normally introduces no significant bias into the flow measurement. Bias could be introduced here if the temperature profile is different than the velocity profile and the temperature sensors are monitoring at locations other than the velocity monitor locations.

Some ultrasonic systems monitor temperature to convert flow in units of actual cu. ft/hr to standard cu. ft/hr. The calculation requires a knowledge of the speed of sound, which again depends on the flue gas composition. Bias can be introduced here if assumptions made for this composition are not valid or not corrected for changing operating conditions.

5.1.1 Differential Pressure Sensing Systems

Differential pressure systems can be designed to measure at single points or at multiple traverse points, using an averaging probe.

As discussed in Chapter 2, for fully developed, uniform flow, only one or two points need to be monitored to obtain consistent velocity values. Pitot tubes that use electronic pressure transducers may be the simplest approach to monitoring an ideal flow pattern. For more variable velocity profiles, an averaging probe may be more appropriate. Figure 5-1 illustrates different techniques used to obtain averaged volumetric flow measurements in differential flow systems.

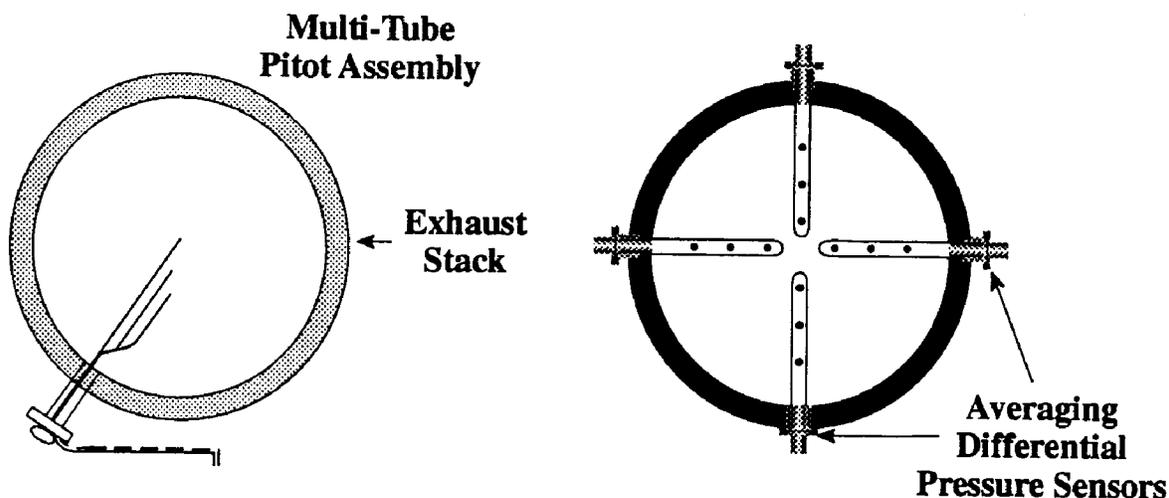


Figure 5-1. Approaches for Obtaining Averaged Volumetric Flow Using Differential Pressure Systems

Differential pressure systems are designed around pressure sensing tubes. Small openings in the tubes sense impact or wake pressures; gas is not extracted into the tube. Bias problems, outside of stratification effects, can occur with respect to these tube openings.

For example, the ideal performance of a differential pressure sensing system requires the flue gas flow to be perpendicular to the tube. If the gas approaches at an angle, the differential pressure between the impact and wake pressure ports will be different. Since the flue gas velocity is calculated from the square root of the differential pressure, the velocity will be biased. The velocity can be biased either high or low, depending upon the probe design and the angle of the flow with respect to the facing plane of the tube.

The flow direction may be non-normal to the tube if (1) the probe is twisted, sags, or oscillates with the flow; (2) the flow itself is swirling; or (3) the flow direction otherwise changes over the cross-section. Swirling, cyclonic flow can contribute to some of the greatest errors in flow measurement, because the angles of attack to the probe are far from perpendicular. Differential pressure sensors are not calibrated to such arbitrary angles, so installation of these systems where cyclonic flow is present should be avoided.

Probe plugging is also of some concern in differential pressure sensing systems. If the probe system is calibrated versus Reference Method 2 over the cross-section, by conducting a pre-RATA as mentioned in Chapter 2, a plugged opening on an averaging probe will not contribute to the pressure average and may cause a bias. Such bias is difficult to quantify. However, with probe blowback systems, probe plugging is rarely a problem. In severe situations the probe blowback frequency and/or pressure can be increased. Condensation of effluent moisture by molecular diffusion can occur in the pitot lines. This problem can be eliminated if the lines are included in the periodic blowback.

Differential pressure system calibration checks are usually performed behind the probe. The checks are designed to test the performance of the pressure transducer, by first sealing off the probe from the system and then pressurizing the remaining plumbing of the system. This procedure does not actually check the probe problems discussed above and serves principally to test for leaks and electronic problems.

5.1.2 Thermal Sensing Systems

Thermal sensing systems monitor the electrical resistance of a heated wire. Flowing gas will cool the wire and change the monitored resistance. Another approach maintains the wire at a fixed temperature and monitors the current necessary to keep that temperature constant. These systems are relatively simple and easy to deploy in arrays across a stack or duct cross-section. A single thermal sensing element suffers the same problems of representativeness in a situation of stratified flow, but when a grid of sensors are deployed at Reference Method 2 traverse points (Figure 5-2), it becomes relatively easy to meet certification requirements (Olin, 1993).

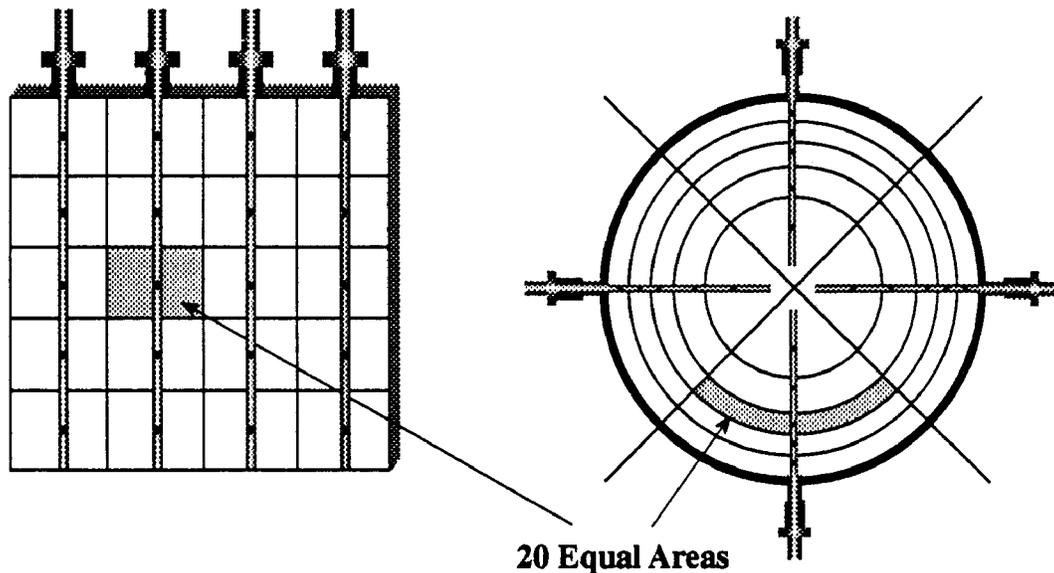


Figure 5-2. A Grid of Thermal Sensors Monitoring at Reference Method 2 Traverse Points

Water droplets will cause errors in thermal sensing systems, since heat from the sensor will be used to evaporate droplets adhering to the sensor. This loss of heat by evaporation is interpreted as heat loss to the flowing gas and will result in a high-biased flow reading. Therefore, thermal monitors are not applicable to flue gases containing entrained water droplets. Thermal sensing systems are also subject to corrosion and particulate build-up. Acid droplets can eat into the metal junctions of probe arrays and cause catastrophic failures rather than systematic bias. Particulate build-up will slow instrument response by forming an insulating layer on the probe temperature sensors. Various stratagems have therefore been devised to minimize this problem. Techniques such as flash heating the sensors (as in a self-cleaning oven), blowing off deposits with instrument air, or designing aerodynamic measuring cavities to reduce accumulation have all been applied.

Calibration checks of thermal sensing systems again do little to check bias problems associated with the thermal sensors themselves. The calibration checks merely test the back-end electronics of the system with simulated signals and do little to indicate potential in-stack bias problems.

5.1.3 Ultrasonic Monitors

Ultrasonic monitors measure on a line, and as has been pointed out in Chapter 4, Section 4.2.2, a line average is not the same as an area average. However, Traina (1992) has calculated that for typical circular stacks, the difference between the two measurement methods will be on the order of 3–5%. This bias can be easily incorporated into the calculation algorithms of the monitor control system.

Problems of stratification are not as straightforward, but can be minimized either by cleverly choosing the measurement path or by adjusting the monitor data to match Reference 2 results through the calculation algorithms.

The choice of measurement paths have been discussed in detail by both Traina (1992) and Kearney (1993). Presented with the problem of measuring volumetric flow in a highly stratified duct, Kearney developed a computer program to match possible measurement paths against the velocity average determined by Reference Method 2. Although this procedure was successful in this application, its success was dependent upon several assumptions: (1) the stratification pattern was stable and independent of load, and (2) the Reference Method 2 data could be correlated with a measurement path not in the cross-section, but at an angle to it (on the order of 45E). The validity of the second assumption depends on the stratification pattern persisting through the duct.

It has been recommended not to site flow monitoring systems in locations where swirling, non-axial flow is present. However, it is often difficult to find such locations where the flow is completely axial. Figure 5–3 shows a typical situation in which the flow is pitched in the upward direction due to a bend in the duct.

For an ultrasonic monitor installed in the plane of the bend, the vector component of flow along the path decreases the sound pulse time of flight to the downstream transducer and increases the time of flight to the upstream transducer. Since the velocity is determined by subtracting the reciprocals of the two times of flight, the flow will be biased high. One solution to this problem, suggested by Traina, is to orient the measurement path so that the monitoring system is perpendicular to the pitch (Figure 5–3). The path measurement will be less sensitive to the effect of the pitch and more amenable to stable correlations and bias corrections. [Note that this siting recommendation is opposite to that recommended for transmissometers (40 CFR 60 Appendix B PS1). Transmissometry is concerned with measuring an effect due to the presence of particulate matter, not velocity.]

In other situations, particularly where two ducts are exhausting into a single stack or the pitched flow is otherwise variable, an "X-pattern" technique is sometimes used. In this

arrangement, two sets of ultrasonic transducers are purported to cancel out the pitch effect. One set exhibits a positive bias with respect to the pitch, the other a negative bias.

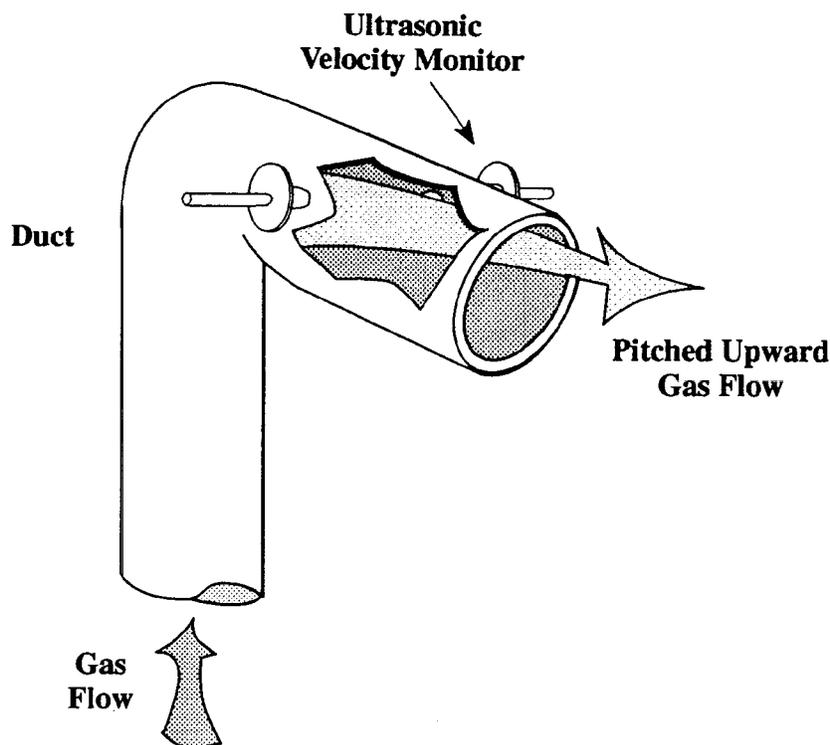


Figure 5-3. Pitched Flow After a Bend

Ultrasonic sensors check their calibration by electronically substituting signals to cross-check the electronics and by introducing a known delay in the pulse. Again, these methods are basically internal electronic checks and are not independent of the system.

Ultrasonic sensors are unique among the flow monitors in that the sensing elements of the system are not located in the duct or stack. However, the transducers can be exposed to the flue gas. Blowers, which pass clean air across the sensors, are designed to keep them clean and free of particulate build-up.

5.2 SUMMARY

The major problems that can produce bias in different types of flow monitors are summarized in the table on page 5-1. Choosing the most appropriate flow monitoring system is highly dependent on the specific characteristics of a particular site. Making the right choice can be the most important step toward avoiding bias problems in the future.

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CHAPTER 6

SOURCES OF BIAS IN THE GAS ANALYZER

Chapter 6 Highlights

Gas Analyzer Problems

| Problem | | Corrective Actions | Page Refs |
|--|---|--|------------|
| Name | Description | | |
| General | | | |
| Interference Effects | The presence of other gas species throws off the measurement of the gas being monitored. | Change analysis technique. Measure concentration of interferent and correct for its presence. Scrub out the interfering species before analysis. | 6-2-6-5 |
| Analyzer Design | Features inherent in an analyzer's physical construction, electronic design, and analytical technique can be prone to producing measurement bias. | Choose analyzers wisely, considering bias-prone features. In QA/QC program, tailor preventative maintenance to design features that are bias prone. | 6-7 |
| Ambient Effects | | | |
| Temperature | If exposed to extreme temperatures, the analyzer may produce erroneous readings. | Temperature stabilize the analyzer. Measure temperature and compensate. | 6-5, 6-6 |
| Pressure | Changes in barometric pressure can introduce systematic error in spectroscopic systems where measurements are made from a sample cell. | Monitor pressure and mathematically compensate for pressure effects. | 6-6, 6-7 |
| Polluted/ Corrosive Atmosphere | Situations like plume downwash or flue gas exhausting into CEM shelter can produce systematic error or system failure. | Shelter or otherwise protect system. Filter ambient air. | 6-6 |
| Calibration | | | |
| Incorrect Gas Values | If the presumed and actual calibration gas concentrations differ significantly, biased measurements will result. | Replace or recertify gas. Find actual concentration. Recalculate effluent concentrations. | 6-8 |
| Inadequate/ Inconsistent Response Time | Bias can develop if operator or operating system does not allow adequate time for monitor to reach its asymptotic value. | Establish procedures that ensure consistently adequate time for monitor response. | 6-9-6-11 |
| System Calibration Obscuring Local Bias | Routine analyzer adjustments during full system calibration can mask local sources of bias. | Perform probe and local analyzer calibration checks in addition to system checks. | 6-11, 6-12 |

CHAPTER 6

SOURCES OF BIAS IN THE GAS ANALYZER

6.1 INTRODUCTION

Bias in CEM systems can originate from the sampling system design, as discussed in Chapters 3 and 4, but it can also originate from the system analyzers. Analyzers used in CEM systems should be able to distinguish between the gas to be measured and the other components, or interferences, of the flue gas mixture. The ability of an analyzer to minimize the effects of interferences depends on the measurement principle employed or on the effectiveness of their removal before the gas is analyzed.

In addition to an instrument's capability for interference rejection, the construction and electronic design of an analyzer can also contribute to its measurement bias. Analyzer sensitivity to environmental factors, drift, response time, and noise, can all affect its performance. However, this performance can be evaluated in part by conducting calibration checks.

Calibration checks should be designed to provide an independent assessment of analyzer operation. In the United States, this independence is achieved by using audit gases traceable to NIST standard reference materials (SRMs). However, internal references, such as sealed gas cells, filters, or reference spectra are also used to check analyzer calibration. Neither a calibration that uses an audit gas nor one based on an internal reference technique is completely independent of the CEM system, and both are subject to measurement biases that can be difficult to detect.

Four sources of analyzer bias, (1) interferences, (2) ambient effects, (3) design, and (4) calibration, can be avoided and usually resolved before, or during, CEM system certification. However, as the system ages, new calibration gases are purchased, or procedures are changed, biases caused by these factors may again enter into the system.

6.2 ANALYZER INTERFERENCE EFFECTS

It is not a trivial exercise to measure the concentration of SO₂, NO, CO₂, or O₂ in the mixture of gases emitted from combustion sources. Although it may be relatively easy to identify and measure the concentration of an isolated compound, it is the presence of other species that challenges analysis techniques. This challenge can be met in a number of ways, either by

1. Employing a technique that is specific to the compound being measured;
2. Measuring the concentration of all of the compounds, or the principal interfering compounds, and correcting for their presence; or
3. Removing the interfering species before analysis.

For continuously operating instruments, the first option is preferred although difficult to achieve. The analysis technique used is also dependent upon the CEM system design. The analysis options are reduced once the type of system is chosen (e.g., extractive, in-situ, dilution, hot-wet).

Typical interferences found in analyzers used for source monitoring are provided in Table 6-1.

Table 6-1. Typical Interferences Found in CEM System Analyzers

| Technique | Typical Interferences |
|---|---|
| Infrared SO ₂ , NO, CO ₂ , CO | H ₂ O, CO ₂ , CO, Temperature |
| Luminescence SO ₂ , NO _x | CO ₂ , O ₂ , N ₂ , H ₂ O, Hydrocarbons (Quenching) |
| Ultraviolet (UV) SO ₂ NO | NO ₂ SO ₂ |
| Electrochemical | Varies with cell EMFs |
| Electrocatalytic ZrO ₂ cells for O ₂ | CO, Hydrocarbons |
| Paramagnetic O ₂ | NO |

6.2.1 Instrument Design

Analyzer manufacturers first attempt to minimize these interferences through the instrument design. For example, in infrared analyzers, where overlapping O₂ and CO₂ spectral absorption bands are a problem, the technique of gas filter correlation can be used to minimize the interference of these gases. Since these spectra do not correlate with those of the pollutant molecules being measured, they merely attenuate the light in both the sample and reference modes of the instrument and do not lead to a bias. Also, the use of in-series Luft detectors has minimized the effect of H₂O and CO₂ interferences in the traditional nondispersive infrared analyzers.

Another example of instrument design being used to minimize interference effects can be seen in the steps taken in SO₂ fluorescence analyzers to reduce quenching effects caused by changes in percent level concentrations of O₂, CO₂, N₂, and H₂O. These changes have been found to cause errors from 5–15% in source-level fluorescence analyzers (Jahnke et al., 1976). The effects can be reduced by using shorter UV wavelengths, or by measuring the sample under reduced pressure. A better approach has been to dilute the sample with air to maintain a relatively constant

background gas from which the SO₂ fluorescence radiation can be measured. Consequently these analyzers have been successfully employed in dilution systems.

6.2.2 Corrections

If the instrumentation cannot be refined to minimize interference effects, the next option is to measure the concentration of the interferent and mathematically correct for its influence. For example, this approach has been taken in second derivative SO₂/NO analyzers, where the SO₂ interferes with the NO measurement. Both are measured and an electronic correction factor proportional to the SO₂ concentration is applied to the NO output. Also, in the electrocatalytic zirconium oxide O₂ analyzers, CO will react with the sampled oxygen to form CO₂ to deplete oxygen concentrations near the sensor. This problem only arises at high CO concentrations, but it can be resolved by measuring the CO concentration and correcting the O₂ output. In paramagnetic O₂ analyzers, NO, which is also paramagnetic, will interfere. Again, this is only a problem at high NO (percent) levels, but can be corrected if the NO is measured.

Other techniques can be applied in infrared and ultraviolet (UV) differential absorption analyzers. In these instruments, a complex spectral absorption curve is obtained of the flue gas. By using computer-maintained library spectra, spectra of the gaseous constituents at different concentrations can be matched until the sampled spectrum is reproduced. This and similar methods have been applied in Fourier transform infrared (FTIR) spectroscopic and differential optical absorption spectroscopic (DOAS) instruments.

In some cases, an analyzer can use an assumed correction factor for an interfering species rather than a measured one. For example, in a base-loaded power plant, CO₂ and H₂O concentrations are relatively stable, and rather than having to install and operate another analyzer to provide a correction factor, an assumed value established under normal operating conditions can be factored into the output. A modification of this method is to use a nomograph or computer algorithm that provides a variable correction factor based on flue gas concentrations (assumed or measured) or unit operating parameters. These corrections are only as good as the assumptions on which they are based and can lead to significant biases under atypical operating conditions. It is under these conditions, however, that accurate pollutant measurements are most desired.

Choosing analyzers for a CEM system requires some knowledge of how they operate and how interfering gases can affect the measurements. Unfortunately, vendor literature does not always provide detailed information on interference effects or methods used to correct for them. When data obtained from the system do not correlate with independent reference method tests or calculations made from plant operating information, further investigation may reveal the assumptions used in correcting the analyzer output.

6.2.3 Scrubbing

If it is not possible to account for interference through instrument design or corrections, the last option is to scrub out the interfering species from the sample gas. This was a traditional technique used in early CO nondispersive infra-red (NDIR) monitoring instrumentation.

Typically, both H₂O and CO₂ were scrubbed out in order to obtain an interference-free CO spectrum. Scrubbing is an adequate solution to the problem if the scrubbing materials are routinely replaced and if they do not remove any of the gas that is to be measured. However, when a major effluent component, such as CO₂, is removed, the sample volume must be adjusted to correct the apparent pollutant concentration measurements.

As discussed in Chapter 3, dilution air used in dilution probes or external dilution assemblies must be free of the compound to be measured. Gas scrubbers are routinely used for this purpose. Outside of this application, few scrubbing systems are used in utility CEM systems since analyzers are available today with enough discrimination to avoid using this last option.

6.3 AMBIENT EFFECTS

The environment in which an analyzer is located can also affect its performance. This is particularly true for in-situ analyzers but also holds true for extractive system analyzers. Ambient temperature, ambient pressure, vibration, and the composition of the ambient atmosphere, all can affect source monitoring instrumentation.

6.3.1 In-Situ Analyzers

In-situ analyzers can be subject to severe environmental conditions. These analyzers are either located on a stack or duct exposed to the atmosphere or in the annulus between the stack and stack liner. In either case, the instrument must be able to function properly through swings in temperature, variable humidity, and sometimes corrosive atmospheres.

Most in-situ analyzers are temperature stabilized and are usually covered with an aluminum or fiberglass hood. They are, however, not commonly air-conditioned, so if the temperature increases beyond specified limits, the instrument signal can drift dramatically or the instrument may simply malfunction. Locating a system on a metal stack, exposed to the sun, or in an annulus where elevated temperatures are commonplace should be avoided.

Effects of stack or duct vibration are not a common problem with in-situ analyzers, despite the frequent statements found in competitor trade literature. Vibrations found in stack installations are usually not at frequencies that will affect an instrument's performance. The manufacturer will otherwise make certain that optical and other system components are secured sufficiently to withstand the vibration encountered. It has been noted occasionally that circuit boards may loosen, but this will generally lead to major system fault rather than development of systematic errors in the measurement system.

In-situ analyzers are exposed to the ambient atmosphere and may be subject to plume downwash or acid liquids condensed from the exhaust gas. Manufacturers will generally seal the instrumentation in sturdy, cast aluminum housings to protect both optics and electronics from these atmospheres. However, continuing exposure to acid atmospheres will require more attention to maintenance and upkeep of the analyzer, particularly to the blower systems and clips and

flanges that are prone to corrosion. Again, problems experienced here will tend not to lead to systematic errors, but rather to system failures requiring corrective action.

6.3.2 Extractive System Analyzers

Extractive system analyzers are commonly located in a CEM shelter that is temperature controlled. The assumption that shelter temperatures are stable may not always be true and can lead to drift problems in the system analyzers. The integrated circuits of the analyzers are temperature sensitive as they are in the in-situ systems. However, the extractive system analyzers, whether source level or ambient, may not be temperature stabilized if it is assumed that they will operate in a temperature controlled environment. In such cases, special care must be taken in sizing the heating and cooling system for the shelter. Inadequate systems can lead to cycling indoor temperatures that can ultimately cause unacceptable drift in the CEM systems.

EPA has not established temperature response performance criteria for CEM system analyzers, although temperature effects will contribute to the daily calibration error, which is limited to $\pm 2.5\%$ of span for system certification. Here, the ISO has established zero drift limits of less than or equal to $\pm 2\%$ and a span drift of less than or equal to $\pm 4\%$ of full scale for an ambient temperature change of $\pm 10^\circ\text{C}$.

The ambient atmosphere must also be considered for CEM system shelters. Although analyzers are better protected in a shelter, introduction of pollutant gases into the shelter can lead to system biases. A problem can occur in some CO_2 infrared analyzers that are constructed with gaps between the measurement cell and the light source and detector. During a certification test, many people occupy the shelter, conducting tests, operations, or observations. With time, the CO_2 concentration in the shelter will increase. If the analyzer is used in a dilution system, the increased ambient levels of CO_2 will be detected by the analyzer to give abnormally high source CO_2 readings and invalidate the test. Similar problems may occur if the sampled flue gas is exhausted into the CEM shelter from the analyzer manifold or if the ambient air drawn into the shelter is contaminated from plume downwash.

Barometric pressure will also have an effect on extractive system analyzers where measurements are made from a sample cell. The pressure of these cells is generally maintained at ambient atmospheric pressure since the gas is sampled from a manifold that exhausts directly to the atmosphere. In many spectroscopic techniques, the measurements are sensitive to the sample cell pressure through pressure broadening of the measured spectra or by changing the density of the gas in the measurement cell. Consequently, to account for altitude, most analyzers incorporate adjustments that are set by the manufacturer after the installation location has been identified.

However, such altitude corrections do not account for day-to-day variation of **atmospheric** pressure. Changes in barometric pressure due to changing weather conditions can have a considerable effect on the analyzer measurements. The error introduced in the measurement is specific to the analyzer and should be obtained from the instrument manufacturer. Unfortunately, this information tends to be difficult to obtain, either because the manufacturer has not quantitatively determined the effects of barometric pressure or does not wish to acknowledge that

the instrument is subject to such an effect. A number of manufacturers are now designing their systems to compensate for barometric pressure changes, or are offering the feature as an option. If it is desired to minimize analyzer drift, this option should be taken.

6.4 ANALYZER DESIGN

Both the physical construction and electronic design of a source monitoring analyzer are important in its operation. Although it is difficult to generalize here, it is noteworthy that today, state-of-the-art analyzers incorporating microcomputer circuitry and microprocessor firmware tend to be much more stable and drift- and noise-free than those constructed ten years ago. A number of analyzer manufacturers have not yet made this transition in technology. The older designs are still serviceable, however, and can meet today's certification requirements, including the bias test requirement.

Other design features are dependent upon the analysis technique used. For example, in differential absorption UV analyzers, lamp stability is an important factor in instrument operation. In infrared analyzers, detector sensitivity is important. These and other factors discussed above determine the quality of an instrument, its capability of meeting EPA certification requirements, and those design features most prone to systematic error. Taking into consideration bias-prone design features when choosing an analyzer can often head off future measurement problems. Careful consideration of analyzer design also allows operators to incorporate into their Quality Assurance and Control Programs preventative maintenance activities specifically tailored to design features that may be particularly susceptible to systematic error.

6.5 CALIBRATION

The periodic calibration of an analyzer is essential to its proper operation. The analyzer's electronics and optics, its response to environmental factors, and in some cases the effects of interferences can be checked through calibration.

Calibration is "the process of establishing the relationship between the output of a measurement process and a known input." In most instruments, it is too difficult to derive concentration values from first principles (e.g., using the Beer-Lambert law*) and in addition account for all of the other variables associated with the instrument's operation (such as electronic/optical design, environmental factors, and interferences discussed above). Instead, the instrument is calibrated so that it will give an accurate response to a known input.

The instrument manufacturer designs an analyzer to respond over a specified range of concentrations and programs in some relationship between the detector signal and the gas

*Many electro-optical instruments dependent upon light-matter interactions incorporate a form of the Beer-Lambert law to obtain gas concentration values. The Beer-Lambert law is a theoretical expression that states that, for light having wavelengths that interact with the gas molecules, the transmission of the light through the gas will decrease exponentially as the concentration of the gas increases.

concentration. This may be a log-linear relationship for an infrared absorption analyzer, or a more complicated relationship, for example a second derivative function. The manufacturer then calibrates the instrument, injecting calibration gases of known concentration and obtaining a response. Instrument outputs are then adjusted to the known inputs to correct for variations of electronic signals, temperature effects, barometric effects, or possibly, interferences. Ideally, the analyzer will then provide an accurate response to the sampled gas after it is installed in the CEM system.

In the 40 CFR 75 CEM rules, the calibration of gas monitoring systems is required to be checked daily. The conditions under which a system was calibrated at the factory will be different than those at the installation location. Those conditions may also change daily. It has therefore been found necessary to check the calibration of a system daily.

6.5.1 Protocol 1 Gases

In the United States, a general policy has been set through the QA requirements of 40 CFR 60 and 40 CFR 75 that CEM systems be checked using calibration gases. More recently in Part 75, the requirement has gone further to specify that gases traceable to NIST SRMs are to be used. The traceability procedures established to do this are given as Protocol 1 (U.S. EPA, 1977a,b; 1993) and the required gases are known as Protocol 1 gases. In Europe, other methods of instrument calibration have been allowed and, as a consequence, European instruments may use sealed gas cells or reference spectra for self-calibration. Regardless of the adequacy of these methods, instruments used in the United States to meet Part 75 requirements must still provide some mechanism to be checked by Protocol 1 calibration gases.

6.5.2 Bias Due to Calibration Gases

Bias can be introduced into an analyzer's response if the calibration gas is not accurate. Protocol 1 gases are required to have an accuracy relative to an SRM of $\pm 2\%$. The capabilities of gas manufacturers to provide accurate audit gases is periodically checked by EPA. These data are published and made available to the CEM user community.

Nevertheless, errors do sometime occur in the preparation of calibration gases. It is therefore prudent for the CEM system technician to cross-check newly purchased gases with other audit gases before they are used. Typically, a calibration gas cylinder is replaced before the cylinder pressure drops below 200 psi. Enough gas should be available to first calibrate the analyzer using the older cylinder gas, and then check the response of the analyzer to an injection of the new cylinder gas. If the response of the analyzer is within 2% of the certification value, the cylinder should be acceptable. If there is concern that the concentration of the gas in the older cylinder has degraded, further checks should be conducted using the audit gases reserved for quarterly linearity checks. Protocol gases provided by another plant or a source testing company could also serve this purpose. If the response differs by greater than 2% of the certified value, the cylinder should be returned to the cylinder gas manufacturer for reverification.

The use of multi-blend gases in dilution extractive systems has added another level of complexity into system calibration, as discussed in Chapter 3. The make-up gas used in the blend, and the average molecular weight of the blend must be considered when cross-checking gases. Since the critical flow rate of gas through a dilution orifice is dependent upon the average molecular weight of the gas, discrepancies will result if the average molecular weights of the compared gases are different (Miller, 1994; McGowan, 1994).

If it has been found that an incorrect cylinder gas value has been used to calibrate an analyzer or CEM system, the data obtained since that calibration will be biased. However, if the correct calibration gas concentration value is subsequently known, the true emission values can be determined. For example, if an SO₂ analyzer had been calibrated with a gas with an assumed value of 950 ppm and it was later found that the actual concentration was 900 ppm, measurements made by the analyzer would be too high.

The corrected concentration would be:

$$C_{corrected} = \frac{900}{950} C_{measured}$$

The measured concentrations would essentially need to be reduced since the original scale accounted too many parts per million for each part present in the sample.

6.5.3 Bias Due to System Response

Bias can occur in other ways in the calibration process. For example, consider that the response to a zero gas or a calibration gas is not always immediate, but will tend to an asymptotic value as shown in Figure 6-1.

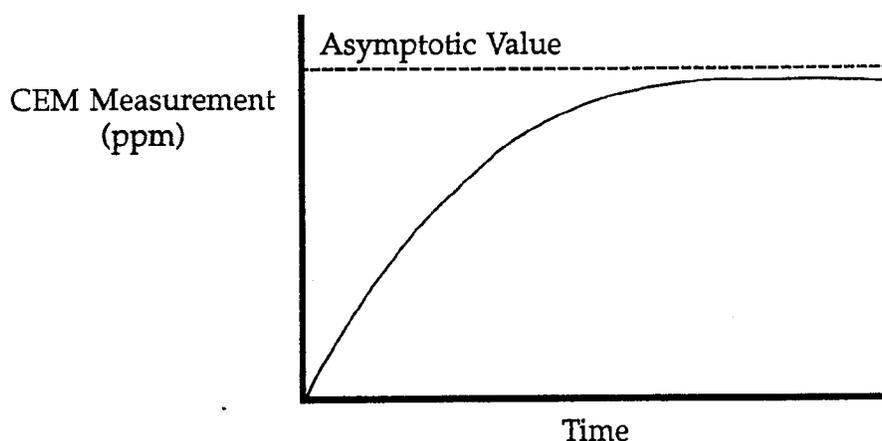


Figure 6-1. Asymptotic Calibration Check Response Curve

The time it takes to reach 95% of the asymptotic value is known as the response time. The system response time is due both to the time necessary for the gas to travel from the probe to the analyzer and the response time of the analyzer itself.

The analyzer response time is often dependent on an integration time, where the signal is averaged or integrated over a period that may range from seconds to minutes in order to obtain a more precise measurement. This period is fixed in many analyzers. However, in others, the integration period may be selected. The response time of many ambient air analyzers used in dilution systems may be on the order of several minutes, whereas the response time of an optical in-situ analyzer may be relatively rapid, on the order of seconds.

If a probe calibration is conducted (as is required in Part 75 for extractive systems and is necessary for dilution systems), the time necessary to flush out the probe and sampling line will enter into the "system" response. At low gas concentrations (e.g., less than 50 ppm), adsorption or desorption of gas on the walls of the transport tubing or sample cell may also delay the approach to the asymptotic value. In the case of adsorption, gas will be adsorbed on to the walls of the tubing, cell, and other surfaces until equilibrium is reached ("passivated"), after which time the cell concentration attains its final value. It may take 15–20 min to reach this value for some systems.

A bias problem develops when the technician or the automatic controller does not allow adequate time for the system to reach its asymptotic value during calibration checks. If the technician waits only 30 seconds before recording a reading on Day 1, but waits 60 seconds before recording a reading on Day 2, a noticeable change may occur in the instrument response. Also, when different technicians use different procedures for adjusting a system, significant biases can be introduced.

The solution to this problem is to adopt automated or consistent manual procedures for the daily calibration error check. In fact, EPA QA requirements specify that these procedures be written and followed. Calibration readings should be taken only after a specified period of time has elapsed. Calibration **adjustments** should be performed only after established QC limits have been exceeded (see Chapter 8). These control limits are also to be included in the written procedure. Frequent adjustments for variations of only a few ppm may serve only to adjust instrument noise and may not actually serve to improve data quality. In fact, the daily, automatic computer corrections for calibration drift performed by some systems may be doing nothing more than adjusting for system noise.

Many analyzers are sensitive to the pressure of the gas in the measurement cell or cavity. In the calibration mode, a high gas flow rate from the calibration gas cylinder can pressurize the cell and lead to subsequent sample measurement biases. In spectroscopic absorption instruments, the gas concentration measured is related to the number of molecules in the light path. If the pressure is increased, the density of the sample gas is increased. The number of the pollutant molecules in the light path increases correspondingly, even though their true concentration remains the same. The gas flow rate into the measurement cell must therefore be the same in both calibration and sampling modes. Since most gas manifolds are maintained to exhaust at a fixed pressure, the flow rates in both the calibration and sampling modes should be set so that this pressure is not exceeded.

6.5.4 System Calibration

In addition to analyzer calibration, one must also consider **system** calibration. The total response from a CEM system is through the "system" and not just the analyzer. As we have seen in Chapters 3 and 4, problems in the extractive system or in-situ monitor interface can also produce biased data. For this reason, the 40 CFR 75 rules require that daily "system" calibrations be conducted so that the combination of analyzer problems, extractive/interface system problems, and data acquisition system problems can be evaluated.

Routine analyzer adjustments performed during system calibration can hide analyzer measurement errors. These can be detected by performing both system and analyzer (local) calibration checks. For example, dilution systems must be calibrated ahead of the point where the dilution occurs. Since ambient air analyzers are used in dilution systems, the calibration gas (at Protocol 1 gas source level concentrations) must be diluted as is the sample gas. The dilution ratio of most dilution systems is determined approximately through selecting the size of the orifice or capillary and by setting an appropriate dilution air flow rate. The system is "tuned," however, by using calibration gas. Imprecise adjustment of the dilution flow rate and errors in the current absolute stack static pressure are all "calibrated out" with the analyzer. Variations in the dilution extractive system may be treated as analyzer drift, corrected by adjusting the span potentiometer or by adjusting the dilution air supply.

Using the analyzers to adjust for the variation of other system parameters can mask what is actually happening in the system. The combined system/analyzer calibration check may mask what is happening in each subsystem. For example, if the dilution probe controls begin to vary too far from their initial settings, there may not be enough adjustment capability in the analyzer potentiometers to bring the system into calibration. One technique that should be routinely applied to dilution systems is to perform a local analyzer calibration check to determine a baseline calibration setting. This baseline value can then be contrasted to the amount of adjustment needed to bring the whole dilution system into calibration. Since ambient air analyzers are used in the dilution systems, permeation tube systems may be necessary for the analyzer calibration check. More conveniently, a low-level concentration CO₂ gas (e.g., 3,000 ppm) could be used to assess the system (Gregoria, 1993).

A particularly aggravating problem can occur in time-shared dilution systems (Figure 6-2). In the system shown, a series of system calibrations would be performed, in turn, through each of the three dilution probes. First, for Unit 1, the analyzers are adjusted for the extractive system as well as analyzer variables. When calibrating the extractive system for Unit 2, the same set of analyzers are then adjusted for the variables associated with the dilution system of Unit 2; likewise for Unit 3. The same analyzers must then meet three separate sets of conditions. The system would then need to be designed to apply a different set of calibration conditions when each unit is being monitored. This could be done through the DAHS, but adds another layer of complexity to the system.

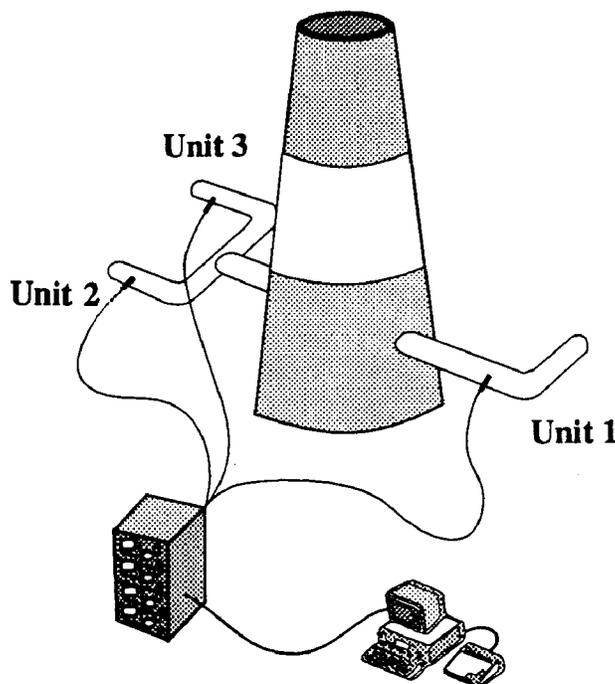


Figure 6-2. Problems in Calibrating Time-Shared Dilution Systems

6.6 SUMMARY

Factors that can cause errors in CEM system analyzers are summarized in the table on page 6-1. Although systematic in nature, many of these errors are variable, depending directly upon changing ambient conditions or levels of interferences. Due to this direct relationship, the resulting biases can in some cases be corrected if these underlying conditions are monitored and taken into account.

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CHAPTER 7

SOURCES OF BIAS IN THE DATA ACQUISITION AND HANDLING SYSTEM

Chapter 7 Highlights

Data Acquisition and Handling System (DAHS) Problems

| Problem | | Corrective Actions | Page Refs |
|--|--|--|-----------|
| Name | Description | | |
| Improper Interfacing | | | |
| Distorted Inputs from Analyzer | Input signals to the DAHS from the analyzer, process controller, or sensors are distorted. | To detect problem, compare DAHS readings to strip chart recorder's. Replace or repair faulty components. | 7-2 |
| Synchronization Problems | Errors will result if system control and DAHS clocks are out of synchronization. | Prior to certification testing, fix any mismatch between system and DAHS clocks. | 7-2, 7-3 |
| Calculation Problems | | | |
| Round-Off Problems | Incorrect rounding methods can produce biased results. | Change math to meet accepted professional practices and the conventions in regulations. | 7-3 |
| Incorrect Parameters | Entering incorrect values for user-configurable parameters will produce recurring errors. | Re-enter correct values. | 7-4 |
| Incorrect Equations | Programming incorrect equations will produce recurring calculation errors. | Require DAHS developers to document and validate all equations and correct code. | 7-4 |
| Improper Correction Routines | | | |
| Automated Zero/Span "Corrections" | Such adjustments may not be warranted and, at times, can introduce errors. | Do not allow automated corrections, OR Require vendor to precisely define and print out each adjustment. Include definitions in QC plan. | 7-5, 7-6 |
| Flow Monitor Correction Factors | If not correlated with actual conditions, these factors can produce systematic error. | Re-test under all prevailing conditions. Then, re-calculate the factors. | 7-6, 7-7 |
| Faulty Dilution System P/T Corrections | Pressure and temperature corrections can produce errors if incorrectly derived. | Require vendor to specify factors used and how derived. Correct if wrong. | 7-7 |
| Bias Adjustment Factor (BAF) | The BAF is a regulatory remedy, not a technical correction for systematic error. | Avoid having to apply a BAF by eliminating the sources of bias. The lower the BAF, the higher the confidence in the CEM's accuracy. | 7-7, 7-8 |

CHAPTER 7

SOURCES OF BIAS IN THE DATA ACQUISITION AND HANDLING SYSTEM

The CEM data acquisition and handling system (DAHS) must also be addressed when considering bias. Biases can occur in manipulating and presenting data as well as in acquiring the data. Unfortunately, today's sophisticated methods of presenting digital data instill an overconfidence in the validity of the computer print-out. The fact that CEM data are presented by a computer, in digital formats, does not guarantee that the data are true and unbiased.

DAHS biases can occur in two ways: (1) by improperly interfacing the analyzers to the DAHS and (2) by improperly programming the DAHS. Interface problems are usually detected prior to or during system certification. Programming problems can be difficult to detect and may appear either during certification or months later, when inconsistencies begin to appear in the data.

7.1 INTERFACING

7.1.1 Analyzer Inputs

A CEM system data acquisition and handling subsystem must interface with the system analyzers. Data must be entered into the computer before it can be manipulated. However, inputs may vary from analyzer to analyzer. Signals transmitted to the computer may be in analog form, or they may be transmitted digitally in newer systems. In these newer systems, analog to digital (A/D) conversion is performed by microprocessors within the analyzer, simplifying signal transmission to the DAHS.

The analyzer signal may be transmitted as current (milliamps) or as voltage (millivolts). When analyzer signals, plant process parameters, and sensor signals for temperatures, pressures, and alarms, are to be received by the DAHS, care must be taken that these input signals are not modified or distorted. The use of drop-in resistors or simple circuits to convert milliamperage current output to a voltage input compatible to the computer may cause shifts or distortions in the signal.

Interface problems can often be detected by connecting a strip chart recorder directly to the analyzer. Time delays, loss of resolution, or shifts in signal magnitude between the strip chart recorder and the DAHS indicate that a problem is present. Such problems need to be resolved during system installation. Although the differences may not appear significant in the mid-range readings of the system, they may become considerably distorted at the high or low values of the range, depending upon the input configuration.

7.1.2 Control System/DAHS Synchronization

A CEM system computer may be used for both system control and data acquisition and handling. Systems that blend supervisory control and data acquisition are known as SCADA (Supervisory

Control and Data Acquisition) systems. This integrated approach can be useful, since the internal status labeling of data (i.e., for calibration, filter purges, and data errors) can be accomplished with one device.

Alternatively, a separate computer may be used for control or programmable logic controllers may be applied for this purpose. In either of these two cases, the controller must be in synchronization with the data acquisition system. That is, if the two systems are running on different clocks, they must at some point provide a means of manipulating or transferring data on the same time basis. If there is a mis-match between these two systems, signal shifts can result. Again, such problems should be resolved during system installation.

7.2 PROGRAMMING

Programming of the DAHS can also lead to CEM system biases. Computational problems or data adjustment algorithms can result in nonrepresentative data. Although the CEM system may meet calibration and audit checks and the computer-generated output may "appear" correct, this does not necessarily mean that the data to be reported will "be" correct. Improper manipulation of the analyzer input signals by the DAHS can generate biases just as well as can measurement failures in the extractive or emission analysis systems.

Calculation problems in the programming are relatively simple to detect and easy to resolve. These problems can arise from round-off errors, the use of incorrect parameters, or the use of incorrect equations. The increasing use of computer QA audit programs (either by EPA or commercial vendors) can help identify these problems relatively quickly.

The internal rounding methods used by the computer and the calculation algorithms can have an effect on the end result. For example, it has been shown that the results can depend upon the calculation order. If, however, calculations are performed using double-precision arithmetic, errors on the order of only 10^{-14} would be expected (Xiao et al., 1993).

Alternatively, if data are truncated or rounded to a smaller number of significant decimal places than are actually measured, a bias can result even if double-precision arithmetic is applied. For example, if a CO₂ reading of 10.2% is obtained by the analyzer and the computer uses a rounded value of 10% in the calculation, a significant discrepancy will result from the otherwise true value.

To prevent errors due to cumulative rounding, EPA policy stipulates that intermediate values used to calculate a final test result should be retained to the maximum decimal precision (at least seven decimal places) supported by the computer used. This is in keeping with accepted professional standards and practice. For example, ASTM Standard Practice E29-90, §7.3 (ASTM 1992) states "When calculating a test result from test data, avoid rounding intermediate quantities. As far as practicable with the calculating device or form used, carry out calculations with the test data exactly and round only the final result."

In user-configurable areas of a DAHS system, parameters such as calibration gas values, F-factors, or other constants can be changed in the calculation algorithms. If improper values are entered, biases will certainly result. For example, if an F-factor is used to obtain values of the emission rate in lbs/mmBtu, any error in the F-factor will be reflected directly in the emission rate calculation. This is generally not a problem for sources burning a single fuel, but for oil/gas, coal/gas, and combined or alternating fuel systems, more attention must be paid to the use of these parameters.

Calibration gas values entered into the DAHS can also affect CEM system data. If the DAHS performs automatic daily calibration adjustments, the data will be adjusted using the calibration gas value input as a reference. If the gas value is keyed in incorrectly, if the wrong value was entered, or if the gas manufacturer incorrectly analyzed the cylinder, a constant bias will enter into the reported data. For these reasons, the cylinder gas values should be cross-checked (as discussed in Chapter 6) and the entered values should be verified.

Equations used in the DAHS programs can also cause system biases. It is not uncommon that programmers, unfamiliar with EPA regulations or the technological basis of CEM systems, will develop the CEM system DAHS programs. Simple errors, such as incorrectly ordering the arithmetic steps of a calculation, programming an exponent as positive instead of negative, or using an equation for a dry-basis calculation instead of a wet basis calculation have all occurred in past programs. Unfortunately, the form of the equation is often buried in the code, and it is difficult for the plant environmental engineer or a CEM systems auditor or inspector to uncover the actual calculations used.

It is therefore necessary for the purchaser of a CEM DAHS to require the DAHS vendor to present in the system manuals or instructions all equations used in the program algorithms. It is also desirable for sources to require DAHS developers to prepare written specifications that explicitly state the equations to be programmed and to include in the acceptance criteria a requirement for independent verification and validation of the code to ensure (1) that the software developer's equations match those in the regulations and (2) that the code correctly implements the equations specified.

7.3 ADJUSTMENT/CORRECTION ROUTINES

The requirement of 40 CFR 75 monitoring plan (U.S. EPA, 1993) to provide equation formats serves as an excellent check for equation validity. However, some calculations are not required to be provided in the monitoring plan and may be proprietary to the CEM system vendor. Pressure and temperature correction routines for dilution probe systems, linearity corrections, etc., are often programmed into the DAHS, but their existence may not be known to the user. Improper correction equations can introduce as much error, or more, as improper report calculations. The following correction routines are those that are commonly encountered:

1. Daily zero/span corrections,
2. Flow monitor system corrections applied for Reference Method 2 correlation,

3. Dilution system pressure/temperature corrections,
4. Linearity corrections/other corrections not accounted for by the analyzer or analyzer microprocessor, and
5. Bias Adjustment Factor (BAF) as required by 40 CFR 75 Appendix A §7.6.5.

7.3.1 Daily Zero/Span Corrections

Two schools of thought exist among CEM system vendors with regard to computer zero/span corrections. The conservative approach is not to allow the computer to perform any zero span corrections using the daily calibration error check (zero/span) data. Instead, the CEM system operator must manually adjust the analyzers after some designated quality control limit has been exceeded (such as 2.5% of span). The other approach is to automatically correct the analyzer data after each daily calibration error check. Automatic corrections are often performed even if quality control limits have not been exceeded. In either case, Part 75 requires that both zero-level and high-level calibration error be determined and recorded before any adjustments are made, whether manual or automatic.

Each approach has its limitations. When no automatic corrections are performed, bias will be introduced (e.g., up to 2.5% of span) if the analyzer is exhibiting a consistent drift. When the system shows a 1% or 1.5% of span drift consistently, then the system may indeed be biased by that amount and it may be worthwhile to adjust the system, even if the control limits have not been exceeded. If, on the other hand, the zero/calibration values are bouncing back and forth between the control limits, only random noise is being exhibited and, over the long term, no bias will be introduced.

Of course, for manual adjustments, more stringent QC limits can be established. CEM technicians become uncomfortable with 2.5% drift limits and frequently adopt a policy of adjusting the system for drift levels as small as 1%. The danger here, of course, is that the technician may merely be adjusting for noise or other random factors, a procedure that is not particularly productive.

For automatic zero/span adjustments, the system may again adjust merely for random noise. The system may appear that it is doing something, but it may be only correcting for random phenomena, producing a result that would be essentially equivalent to one in which the corrections were not performed. However, if the daily zero and span values exhibit a consistent drift or are consistently high over a period of time (such as when a change of barometric pressure due to a weather front affects the system), the automatic correction may indeed be useful in minimizing the bias associated with the condition.

Several additional problems occur with automatic zero/span correcting systems. The most significant of these is knowing the starting point from which you are correcting. If an automatic correction is performed, the computer should print out the amount of correction (either in terms of ppm, percent of span, or both). The reference point for the correction should also be made clear. That is, is the correction made from the previous day's value, or is the correction cumulative, being made from the original zero and span gas settings? The cumulative correction

is preferred—if the drift value refers to drift from the adjusted values of the previous day, automatic adjustment upon automatic adjustment could add up so that one may have drifted less than 2.5% on any one day, but the cumulative drift from the original setting may far exceed a 2.5% drift limit. It is important, therefore, that the operator be able to access the true, raw measurement data versus the "compensated data" in order to double-check if control limits are being exceeded.

Automatic drift corrections have often been a matter of some confusion to CEM system users. It is therefore imperative that the CEM vendor explain to the user what is actually being done in the adjustment and that that explanation be included in the CEM system QC plan.

Another disadvantage to automatically correcting for zero and span drift is that a strip chart recorder connected directly to the analyzer will not read the same as the computer. If the strip chart record is taken directly from the analyzer output and used to verify system performance, this record should first be compared to both the raw and compensated DAHS data.

7.3.2 Flow Monitor System Corrections

As mentioned in Chapter 5, problems of stratification in flow monitoring systems are frequently accommodated by introducing correction factors into the flow monitoring calculations (Stahlschmidt, 1992; Traina, 1992). This practice is common to all of the flow monitoring techniques: differential pressure, thermal, and ultrasonic. Such corrections are valid under the conditions in which they were originally developed. If the correction factor is established at only one load condition and the flow pattern varies under other conditions, the factor may not be valid. If a correction algorithm is developed under low, mid-range, and high load conditions, the adjustments may be shown to be valid over this range of load conditions.

The introduction of system bias in this type of correction can occur also if the source tester performed the reference method with an uncalibrated pitot tube. If a pitot tube calibration factor, C_p , of 0.84 was assumed (as is allowed by EPA Reference Method 2), a positive bias of 6% could result if the actual calibration factor was found to be 0.79 by wind-tunnel testing. Also, if the Reference Method 2 tests were not performed correctly and carefully or were performed carefully but did not traverse across areas of stratified flow, biases could be again introduced. For example, a common procedural error occurs when the tester fails to determine the proper pitot tube alignment at each point by measurement of the null yaw angle. Incorrectly aligning the tube to achieve the maximum response introduces a 5–7% bias in the reference velocity measurements. The S-type pitot tube used in Reference Method 2 is also sensitive to pitch angle bias (i.e., when it sags). Other types of pitot tubes, such as the 3-D pitot tube described in EPA Method 1 and draft Method 2F, can overcome this problem.

The practice of obtaining correction factors for velocity by conducting a so-called "pre-RATA" prior to the actual certification is widespread. However, if the correlation is not performed with some insight and the correction factor is not constant with changing flue gas conditions or with time, the system may fail semiannual/annual performance testing. Since a pre-RATA is not allowed prior to the semiannual/annual RATA, some element of risk exists in the practice.

7.3.3 Dilution System Pressure/Temperature Corrections

As discussed in Chapter 3, dilution extractive systems apply corrections for changes in absolute stack pressure and, in some cases, stack temperature. Correction algorithms are applied by most dilution/extractive system vendors to improve measured system accuracy. However, many vendors view these algorithms and correction factors as proprietary and do not readily share data on their development with users. Others use only the theoretical expressions, not experimentally derived correction factors. In some cases, the expressions used for these corrections have been wrong. Although the errors here are not great and may have been acceptable for other applications, the importance of Part 75 CEM data accuracy requires attention to this issue.

7.3.4 Linearity/Other Corrections

Other correction algorithms may sometimes be applied in the DAHS. For example in some systems, the gas analyzers consist of merely the sensing elements (i.e., lamp, sample cell, and detector) and the DAHS performs all of the signal manipulation. This manipulation may include signal linearization as well as zero/span adjustments. Here, the distinction between the DAHS and analyzer is blurred. In most systems, this function would be handled internally by the analyzer circuitry or analyzer microprocessor.

This type of system design increases the difficulty of system troubleshooting. In these systems, the DAHS programming becomes more complicated due to the addition of analyzer signal control and manipulation functions as part of the data handling requirements. Biases that may be introduced by the analyzer itself may become difficult to detect.

7.3.5 Bias Adjustment Factor (BAF)

The bias adjustment factor has been discussed in Chapter 1 (see Eqs. 1–8 and 1–9). Here, in considering sources of bias in the data acquisition and handling systems, it is important to clearly reiterate the purpose of the BAF. The BAF is a regulatory remedy, not a technical adjustment factor. It was adopted by EPA in direct response to an industry proposal to provide a compliance alternative to elimination of the sources of systematic error in situations where corrective actions were unusually difficult or expensive. As such, the BAF serves a twofold purpose: It provides flexibility in compliance options and, at the same time, serves as a safeguard against reporting artificially low emission measurements that nevertheless meet regulatory requirements for relative accuracy. For example, if a relative accuracy of 10% were permitted without a corresponding bias test and bias adjustment requirement, data that were systematically low relative to the standard but meeting the relative accuracy specification, would be acceptable (as in 40 CFR 60). However, this would give an acid rain trading allowance advantage to a source with a low-biased CEM system; the source would be reporting emissions lower than true and could possibly trade allowances that should not have been.

In any case, the BAF should not be viewed as a multiplier that the DAHS employs to correct CEM system bias. From a measurement standpoint, it is always preferable to eliminate all sources of bias in the CEM system and, thereby, completely avoid having to apply a BAF at all. The next best alternative is to minimize the sources of systematic error and, in so doing, minimize the value

of the BAF. This may require care in system design, installation, and certification. But in general, the lower the BAF, the higher the confidence in the accuracy of the CEM system data.

7.4 SUMMARY

Problems that can occur in the generation of CEM system data by the DAHS are summarized in the table on page 7-1. Many of the errors can be readily corrected once the problem is uncovered.

A number of these problems can be detected through the application of computer data validation programs. These audit programs, or routines, are being developed by EPA for validation of Part 75 data submitted to the agency (Moritz et al., 1993). Routines are also being developed by commercial programmers. In either case, a common technique used is the development of a test data set that contains traps and errors designed to challenge the CEM DAHS. If the DAHS correctly produces summary data from the test dataset, there is increased assurance that those algorithms checked by the audit program are satisfactory.

Computerized audit programs that check all CEM system algorithms are unquestionably difficult to design. Manually checking the DAHS for accuracy and system logic against known parameters should still be conducted using actual sampled data.

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CHAPTER 8

BIAS AND QUALITY ASSURANCE PROGRAMS

CHAPTER 8

BIAS AND QUALITY ASSURANCE PROGRAMS

The ability of a CEM system to provide data representative of "true" emission values depends not only on the design and installation of the system, but also on the adequacy of the CEM system QA program. Although most bias problems will occur during start-up and certification, some problems develop over time. It is the role of the QA program to prevent such problems from developing and to detect them when they do.

8.1 MANAGING BIAS

The goal of the CEM system owner and operator is to maintain optimum performance of the system. This goal can only be achieved by instituting a **working** QA program.

A CEM QA program is required in both 40 CFR 60 Appendix F and 40 CFR 75 Appendix B. These regulations specify that the CEM system owner must develop a QA plan that includes QC procedures for system calibration, preventative maintenance, and system and performance audits. Practically, this means that a QA manual that embodies the plan is to be written. Unfortunately, the QA manual is often viewed as a task that, once completed, can be ignored for the pursuit of more interesting activities. This is not how a CEM program should work. If the CEM system is not routinely inspected, maintained, and audited, the system will degrade, bias will enter into the system, and the data generated will no longer be valid.

Detailed information on developing CEM system QA programs can be found elsewhere (e.g., U.S. EPA, 1977; Jahnke, 1984; Jahnke, 1993; EPRI, 1993). A number of essential points relevant to minimizing bias are summarized here. In the continuing operation of a CEM system, bias can be minimized by following five essential steps:

1. Develop a QA plan that provides for a minimum of three levels of QC:
 - a. Calibration and inspection,
 - b. Preventive maintenance, and
 - c. System and performance audits.
2. Write a QA manual that embodies the plan.
3. Implement the plan.
4. Periodically update the plan and the manual.
5. Record and report.

These five steps can be followed only if the QA program has the support of management, specifically, upper management. QA programs cost money. They take manpower to implement, they

take time, and they require resources. These can be provided only if management is willing to provide them, hence the need for management support.

But let us imagine that a QA program has been developed, the manual written, and the QC procedures implemented on a routine basis. These QC procedures will generate a great deal of information, and this information can be used to assess the quality of the data generated by the system. One does not just **do** QC procedures for the sake of doing them, but rather the information obtained is used in the work of the CEM operator. The CEM operator, technician, or auditor is continually looking for evidence of developing biases or system problems.

Fortunately, many useful techniques are available to aid in this search. One of the most powerful is the use of the quality control chart (U.S. EPA, 1976). In this simple technique, daily calibration values are plotted (Figure 8-1).

Control limits are set, which if exceeded, require action. For example, QC limits can be set at 5% for the out-of-control limits for daily calibration error. Most technicians prefer to set lower limits, however, so that action may be taken before the out-of-control limits have been exceeded.

QC charts can be used to detect trends in system performance. A shift in daily calibration drift values may indicate the onset of system bias. A periodic pattern of drift may indicate the effect of nighttime/daytime temperatures on the system. A correlation of control chart data with barometric pressure may indicate that the system is subject to changes of pressure due to incoming weather fronts.

The data obtained from the QC activities are a valuable resource for maintaining data quality. Data should be collected, charted (when applicable), reviewed, and reported. It is useful for more than one person to review the data, since subtle clues to system performance may be more apparent to an independent, unbiased eye, than to one who has been working closely with the system.

Fortunately, CEM system vendors are becoming aware of the utility of incorporating diagnostic routines into the CEM DAHS (White, 1993). QC charts can be generated automatically in such systems, relieving the technician of tediously tracking and entering daily calibration data. In computerized maintenance packages, warnings of equipment malfunction or deterioration can be provided or preventive maintenance schedules can be called up to organize one's program of daily or weekly activities. These features allow for better organization and record keeping and can reduce the hours spent in the CEM system QC activities.

8.2 DETECTING BIAS THROUGH INDEPENDENT MEASUREMENT

Detecting bias in CEM systems requires both independent measurement and common sense. Independent measurements are obtained by applying methods that are not equivalent to those used by the installed CEM system. Various levels of independence are provided by the mandated EPA CEM performance audit procedures. On the other hand, "common sense" is more difficult to define, but it is essential in uncovering and resolving bias problems.

Techniques used to check or audit CEM systems include:

1. Repeating the certification test RATA;
2. Conducting modified relative accuracy tests using manual or automated reference methods;
3. Testing, using portable inspection monitors;
4. Auditing, using independent standards [cylinder gas audits (CGAs), calibration error tests, linearity checks, and opacity monitor zero jig filters]; and
5. Predicting emissions from plant operating parameters.

These techniques are commonly incorporated into CEM system QA plans as performance auditing procedures. Control limits have been established for such audits in both Appendix F of 40 CFR 60 and Appendix B of 40 CFR 75. If these control limits are exceeded, the data may be compromised for regulatory application. For example, for a Part 75 SO₂ monitoring system, if the relative accuracy requirement of 10% is exceeded in an audit, the system is considered to be out-of-control. Or, in a quarterly linearity test, if the error in linearity exceeds 5.0% from a the Protocol 1 gas reference value, the system is also out-of-control. Any data taken from the hour of the completion of the audit is unusable and the Administrator may decertify the system (U.S. EPA, 1993). These audit procedures have been discussed extensively in the literature (see for example, Jahnke, 1993; Plaisance and Peeler, 1987; Reynolds, 1984, 1989).

From a diagnostic viewpoint, the mandated audit methods may be somewhat limited. An ideal audit method should be able to uncover biases in the installed CEM system. In order to do this, the method should provide:

1. An independent means of sampling the flue gas,
2. Analytical techniques different than those used by the CEM system, and
3. Separate sets of certified standards—one for calibrating the CEM system and the other for calibrating the audit method, or for auditing the calibration of the CEM system.

If the CEM system uses a procedure or analytical method, **A**, then the audit method should use a different procedure, **B**, if it is to search for system biases. If the procedures are the same, then

the same bias may occur in both the installed CEM and audit systems and the bias will not be detected.

The idea here is for the CEM system to produce data that are representative of the source emissions, i.e., data that are as close as possible to "true" values. Choosing or designing an audit procedure that is similar to that of the installed CEM system may minimize the determination of bias, but may not maximize the determination of truth. In effect, reducing the independence of an audit method to minimize bias may, in fact, mask bias or generate bias. Table 8-1 summarizes the independence of various auditing methods, which are discussed further below.

Table 8-1. Independence of Typical Auditing Methods

| | Sampling Method | Analytical Method | Calibration Standard |
|---|------------------------|--------------------------|-----------------------------|
| CEM System | A | A | A |
| Ideal Audit | B | B | B |
| RATA - Gases | B | A or B | B |
| RATA - Flow | A or B | A or B | A or B |
| Cylinder Gas Audits (Calibration Error, Linearity, CGAs) | A | A | B |
| Opacity Audit Jigs/Flow-Through Gas Cells | A | A | B |
| Calculations from Plant Parameters | B | B | B |

"A" represents the method used by CEM system.

"B" represents an audit method that is independent of Method A.

8.2.1 RATA for Gases

Sampling Method

The RATA used for certification and subsequent semiannual or annual audits requires the use of either a manual reference method (e.g., Methods 3, 6, and 7) or allows the use of instrumental Reference Methods 3A, 6C, and 7E. Test procedures require that the reference method sample from a minimum of three points, 16.7%, 50.0%, and 83.3% of the distance of a sampling cross-section diameter. The sampling method will therefore be different than that of the CEM system installation, unless the CEM system samples also at these three test points.

In cases of severe gas stratification, sampling at the minimum three points may not be satisfactory for determining all biases. In such instances, a complete Method 1 traverse might be necessary to compare a "truer" reference method determination to the CEM system data.

Analytical Method

EPA does not require in either 40 CFR 60 or 75 that the analytical method used in a RATA be different than the one used for the installed CEM system. Technically, a dilution probe–dilution probe comparison, or a fluorescence monitor–fluorescence monitor comparison is acceptable. Other testing specifications may require that different methods be used (e.g., ISO 7935, 1989). However, as noted in Example 1, depending on the systems, either extractive system biases or analytical biases could be masked in the comparison.

On the other hand, if two different methods are used and the results disagree, the question then arises as to which one is correct. The use of a different method for auditing may in itself introduce bias. For example, if the source tester uses a source-level, dry-basis extractive system to perform Reference Method 6C, the chiller may scrub some of the SO₂ from the sample stream to give a lower result than true. If the sampling system bias measurements fail to correct for the SO₂ loss completely, the CEM system would be considered to be reading high since the reference method results are used as a "reference."

If inconsistent results are obtained between analyzers that employ different monitoring techniques, interfering compounds may be causing the problem. Method 6C does, however, require that the source tester conduct an interference check at a typical source at which the Method 6C analyzer will be used. For SO₂, this check is performed by comparing the instrumental method against a modified form of the manual EPA Reference Method 6. Problems sometimes arise when the source testing firm neglects to conduct this required part of Method 6C.

Problems also occur when the reference method testing is performed incorrectly or sloppily. In such circumstances, the instrumental reference methods are subject to many of the same biases as discussed in this *Guide*.

Calibration Standards

EPA does require that a different set of certified calibration gases (Protocol 1 gases) be used than those used to calibrate the CEM system. The standards used are therefore independent.

8.2.2 RATA - Flow

Sampling Method

In flow monitoring systems, the sampling method may be similar to that used in Reference Method 2 or it may be different. Averaging differential pressure sensing systems may have a sensing port located at each Method 2 traverse point. Thermal sensing systems may also have sensors arrayed at the same reference method points. In these cases, it would be expected that the flow monitoring system would compare well with EPA Reference Method 2.

In many systems, however, the flow monitoring points are different. One or two pitot tube sensors or only a few thermal sensors may be used for monitoring the flow. Also, the line averaged measurements made by the ultrasonic sensing systems give equal importance to each point on the measurement line, not to the points of equal area as in the reference method. Nevertheless, these systems can give satisfactory results if the flow is relatively uniform at the cross-section and/or suitable correction factors are introduced.

In practice, the problem of sampling bias is often eliminated through the practice of conducting a pre-RATA or diagnostic test to obtain bias correction factors before certifying the system. Bias may still exist, but more importantly, the validity of the calibration factors depends on their constancy. If they vary over time or do not account for variation of operating conditions, data generated may not be accurate. Such problems would most likely be identified at the time of the semiannual/annual audit. Note that a pre-RATA or diagnostic test should NOT be conducted prior to a mandated semi-annual/annual audit, since readjusting the system prior to audit is neither a technically valid nor an acceptable procedure from a regulatory standpoint.

Analytical Method

The S-type pitot tube is used in EPA Reference Method 2 to measure flue gas velocity. Automated differential pressure sensing systems, being either arrays of pitot tubes connected to a pressure transducer or other averaging devices, utilize the same technique. Although the analytical technique is similar to the reference method, the sensing configurations may be different than those used in the reference method. Thermal sensors and ultrasonic sensors utilize different analytical techniques.

In general, bias introduced by the flow monitoring technique is also calibrated out by conducting the pre-RATA test and correcting subsequent data. Essentially, the cause of any bias, due either to sampling configuration, velocity stratification, sensor angular dependence, etc., is not addressed. The bias is merely accepted and corrected.

Calibration Standards

The S-type or 3-D pitot tubes should be calibrated in a wind tunnel with reference to a standard pitot tube. If the installed flow monitoring system bias is adjusted using data from a pre-RATA test, the flow monitoring system will no longer be independently calibrated. If the same pitot tube used to perform the pre-RATA is used in subsequent RATAs, calibration bias can remain undetected. In such cases, other pitot tubes should be used, or independent test procedures should be designed to check for consistency.

8.2.3 Cylinder Gas Audits (CGAs, Calibration Error, Linearity)

As discussed in Chapter 6, the accepted method of calibrating, or checking the calibration, of a CEM system is to inject calibration gases into the analyzer. For extractive systems, it is required to inject the audit gas at the probe tip, rather than at the analyzer injection port. The intent here is to challenge as much of the CEM system as possible in order to detect both system and analyzer problems. If the calibration gas is injected at the analyzer port, virtually all that is being done is to compare the concentration of the audit gas to the gas used to calibrate the analyzer. However, if the audit gas is injected at the probe tip, system leaks, adsorption effects, and absorption effects might be detected.

Gas audits are limited in what they can reveal about CEM system bias. Because the same CEM sampling system and analyzer are used to determine the value of the audit gas, the auditing method is not completely independent. In fact, once certified, most CEM systems will easily pass a cylinder gas audit. This has been repeatedly reported in the literature (Osborne and Midgett, 1977; Van Gieson and Paley, 1984; Walsh, 1989; von Lehmden and Walsh, 1990).

A CEM technician may, however, wish to extend the mandated gas audit procedures for diagnostic purposes. Some typical examples are:

1. Challenge the CEM system with audit gas both at the probe and at the analyzer port. If the two results do not agree, a problem exists that requires resolution.
2. For dilution systems that use the dilution air as instrument zero air, check the system zero using cylinder zero gas. If the dilution air is contaminated, using an independent source of zero air should uncover the problem.
3. In systems in which the span and/or audit values are considerably higher than the normal range of emissions being measured, use an audit gas corresponding to the average stack gas concentration of the pollutant(s) being measured. Satisfactory results at the lower levels will give increased confidence in the system data.
4. In dilution systems, use permeation tubes or low-level standards to check the ambient gas analyzers independently of the dilution system.

8.2.4 Opacity Audit Jigs/Flow-Through Gas Cells

Methods have been devised for checking the calibration of path in-situ analyzers. Audit jigs, devices that can be placed on the transceiver of a double-pass in-situ monitor, are most commonly used for this purpose (Figure 8-2).

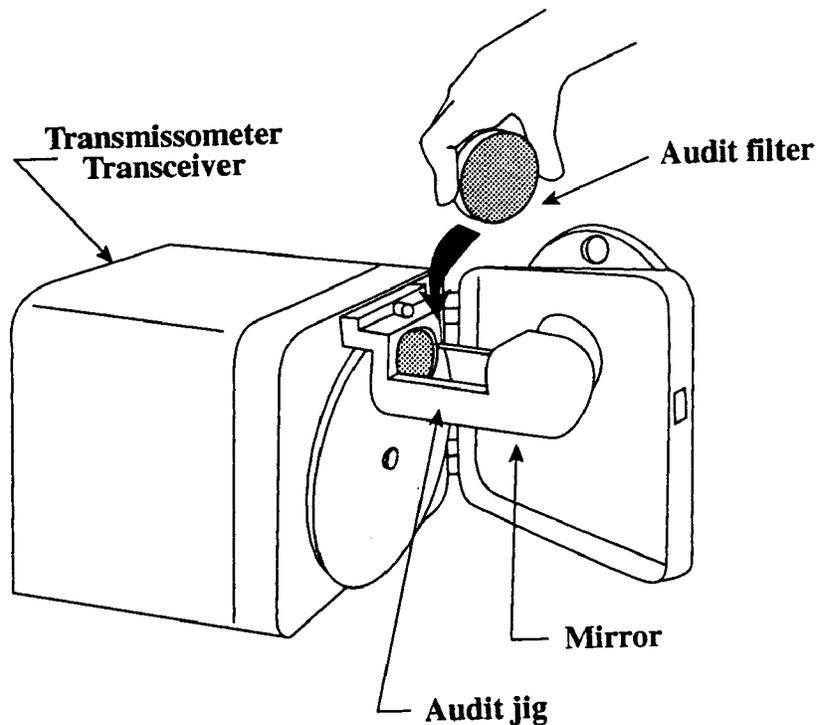


Figure 8-2. A Transmissometer Audit Jig

Transmissometer jigs consist of a slot for holding calibration filters and a short-range retroreflector assembled into a holder that can be attached onto the transceiver. The device and transceiver basically constitute a "mini-transmissometer" that can accommodate audit calibration filters. Certified filters can be placed between this retroreflector and the transceiver head to check the calibration of the instrument over a range of opacities. Detailed guidance for conducting a transmissometer performance audit can be found in Plaisance and Peeler (1987).

Audit gas cells can be used similarly to evaluate instrument performance. The audit gas cell is attached to the transceiver of the double-pass system (Figure 8-3).

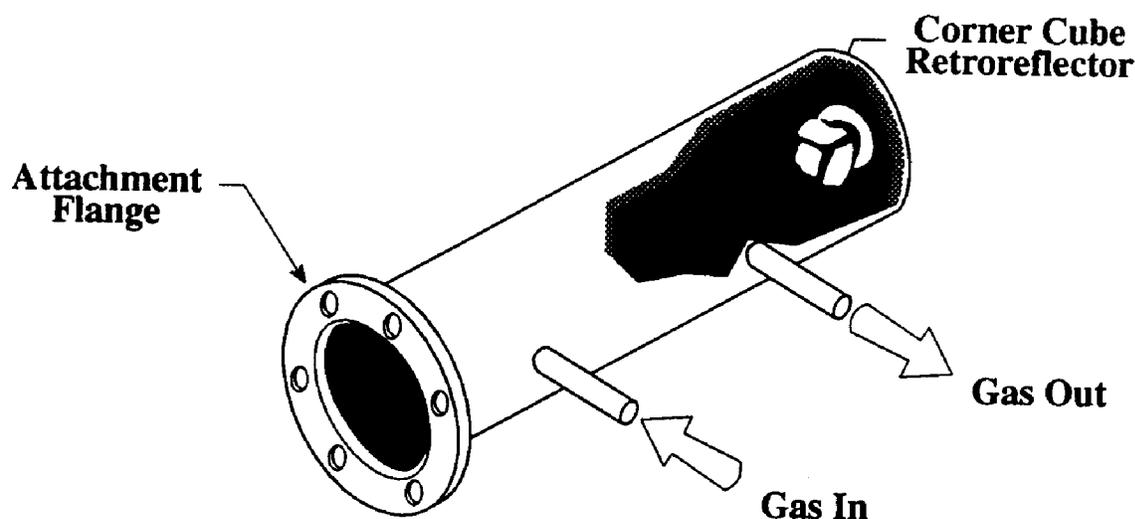


Figure 8-3. Audit Cell for an In-Situ Double Pass Gas Analyzer

As with internal flow-through gas cells (Chapter 4), audit gases, chosen for the appropriate optical depth values, can be used to evaluate the system.

Neither a transmissometer audit jig nor a gas monitor audit cell checks the absolute accuracy of the measurement system. Again, the audit method is not totally independent of the system, because the transceiver of the installed system is actually performing the measurement. Only the measurement standards are independent, as is the case in using audit gases in an extractive gas monitoring system.

There are many other factors involved in cross-stack measurement, such as system alignment and the viability of the cross-stack zero, that cannot be checked using audit jigs or gas cell audit checks. The use of audit jigs may, however, point out problems that affect the measurements, such as optical or electrical problems of the transceiver. One of the most common problems found through the use of transmissometer audit jigs is the incorrect determination of stack exit correlation factors. These factors are used to correct the in-stack opacity measurement to the stack exit values. The necessity for the auditor to calculate correction factors for the audit filters frequently reveals errors in the original determinations for these values.

8.2.5 Calculations from Plant Parameters

A diagnostic tool that should not be ignored is the calculation of emissions values from plant operating parameters. Using information such as fuel sulfur content, fuel feed rate, fan speed, etc., emissions can be at least grossly estimated without conducting an emissions measurement. These estimates can then provide a first-cut consistency check for the instrumented data.

The advantage of this technique is that it is completely independent of the monitoring system and can point out potential CEM system problems that might otherwise have been masked by the non-independent features of other audit methods. The problem with determining emissions from

plant parameters is that many assumptions are necessary in the determination of a complex model must be developed to characterize the emissions. The assumptions used must then be valid and the calculations, or the model, must remain valid under varying operating conditions. Another limitation of this approach is that the values of the input parameters may not be precisely known, e.g., the coal sample is often not representative of the actual fuel fired or the laboratory-determined sulfur content of the fuel is imprecise.

Furthermore, the calculated values are only estimates, not direct measurements. Rarely are these estimates and their underlying models rigorously validated to provide a high degree of confidence in their accuracy.

Nevertheless, important generic information on CEM system performance can be obtained by modelling or calculating emissions. If the results do not agree with the measured emissions, the problem may rest either with the calculation or with the CEM system. Although the results may be equivocal, the resolution of the problem may lead to greater insight into the CEM system and plant operations.

8.3 DETECTING BIAS BY USING COMMON SENSE

From a less technical standpoint, it should be understood from the above discussions, that there is no one way that CEM system bias can be determined. Mandated methods provide the impetus for performing certain audit checks, but these checks do not examine all the possibilities where bias might occur.

Obtaining accurate, precise, and unbiased data requires both common sense and intellectual honesty. The goal is not to obtain the lowest possible values for the relative accuracy or the bias correction factor, but rather to obtain the **true value**. Because the true value is usually never known, one must check and cross-check both the CEM equipment and data to gain confidence that bias has been eliminated.

The process of checking and cross-checking is the work of a detective; one must look for clues and leads that may indicate a system problem. It is necessary to maintain objectivity: accepting a result not just because it agrees with one's preconceptions, but because it makes "sense." Rounding off numbers in one's favor, modifying audit methods to give a better result, or selectively reporting data are counter-productive exercises when attempting to uncover bias. Common sense and objectivity must be exercised in both monitoring and auditing in order to build an overall confidence in the monitoring data. Often, it is only over a period of time that the necessary experience is gained before this is understood.

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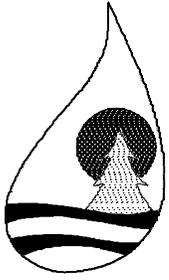
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POSTER

ELIMINATING BIAS IN CEM SYSTEMS

—

A CHECKLIST



**U.S. Environmental Protection Agency
Acid Rain Division**

Eliminating Bias in CEM Systems

—

A Checklist

How to Use this Checklist

- Step 1:** Identify the type of components in your monitoring system.
- Step 2:** For each component in your system, find the potential causes of bias as shown in the Checklist. Refer to the indicated pages in the "Operator's Guide" for additional information.
- Step 3:** Diagnose the components in your system using the list of possible causes shown in the Checklist. Narrow in on the source of the measurement bias.
- Step 4:** Take corrective action.
- Step 5:** Re-test for bias. If necessary, take further corrective action until the source of bias is eliminated or brought within acceptable limits.

Chapter 2 Highlights

Probe Location and Stratification Problems

| Problem | | Corrective Actions | Page Refs |
|---------------------------------|---|--|------------|
| Name | Description | | |
| Stratification — All Types | Gas stratification and flow stratification produce unrepresentative sampling and bias measurements during Relative Accuracy Test Audit. | <p>Find unstratified locations if at all possible.</p> <p>Use fans or gas reinjection to solve gas stratification problems.</p> <p>Use straightening vanes or baffles to solve flow problems.</p> | 2-9 |
| Stable Stratification Patterns | Stratification is present but pattern does not vary over time, i.e., with load or process changes. | <p>Sample at a point representative of the area of measurement.</p> <p>Monitor on a path representative of the area of measurement.</p> | 2-9, 2-10 |
| Varying Stratification Patterns | Stratification is present and pattern varies as plant's operating conditions change. | <p>Calibrate the monitored values to the reference values determined over the range of variation (e.g., different load/process conditions).</p> <p><u>For point sampling systems:</u> Extract or monitor at multiple points.</p> <p><u>For path sampling systems:</u> Monitor on paths less sensitive to variation.</p> <p>Monitor on multiple paths on the cross-section.</p> | 2-10, 2-11 |

Chapter 3 Highlights

Sampling System Problems — Extractive CEMS

| Problem | | Corrective Actions | Page Refs |
|---|--|---|------------|
| Name | Description | | |
| Probe Problems — Source Level Systems | | | |
| Plugging | Particulate matter clogs sampling probe. | Blowback. Increase filter surface area. | 3-3, 3-4 |
| Scrubbing | Precipitates on probe "scrub" SO ₂ from sample gas. | Blowback. Redesign. | 3-3, 3-4 |
| Probe Problems — Dilution Extractive Systems | | | |
| Pressure Effects | Pressure changes affect dilution ratio causing measurement errors. | Calculate correction. | 3-5, 3-6 |
| Temperature Effects | Temperature changes affect dilution ratio causing measurement errors. | Calculate correction. Add probe heater. Replace with ex-situ probe. | 3-5, 3-6 |
| Droplet Scrubbing | Evaporation of droplets in sonic probe can plug probe or cause pre-diluting and inconsistent measurements. | Attach demister. Replace with ex-situ probe. | 3-5 |
| Multi-Component Cal Gas Effect | Mixtures of cal gases may alter the expected gas velocity through the sonic orifice, biasing measurements. | Calculate correction. Use gas mixtures consistently. | 3-6–3-8 |
| Contaminated Dilution Air | Trace amounts of measured gas in dilution air cause errors. | Check zero baseline with high quality zero air. | 3-9 |
| Varying Dilution Air Pressure | Poor quality dilution air regulator adversely affects dilution ratio. | Install flow controllers or better quality pressure regulators. | 3-9 |
| Other Sampling System Problems - Source-Level Extractive Systems | | | |
| Water Entrainment | Collected liquid can scrub soluble gases, dilute sample gas, or cause leaks through corrosion. | Redesign. | 3-9, 3-10 |
| Leaks | In negative pressure systems, leaks may dilute sample gas. | Find and remove leaks. | 3-10, 3-11 |
| Adsorption | Gas adsorbs on walls of tubing causing measurement errors, particularly at low emissions concentrations. | Increase flow rate. | 3-11, 3-12 |
| Absorption | Gas is absorbed in moisture condensed in the H ₂ O conditioning system. | Remove moisture. Acidify condensate. Change system design. | 3-12, 3-13 |
| Moisture Monitor Errors | Systematic error in moisture monitor may produce bias. | Factor in error from moisture monitoring in test calculations. | 3-13 |

Chapter 4 Highlights

Sampling System Problems — In-Situ Gas CEMS and Opacity Monitors

| Problem | | Corrective Actions | Page Refs |
|--|---|---|--------------|
| Name | Description | | |
| Point Monitors | | | |
| Blinding | Precipitate on the filter seals the probe tip from the flue gas. | Clean or replace filter. | 4-4 |
| Faulty Audit Gas Injection | Improper flow rate of calibration gases results in biased concentrations in probe cavity. | Adjust flow, carefully following calibration procedures. | 4-4 |
| Temperature Distortions | If temperature sensors are not working properly, errors can result in emission values. | Calculate correction. Adjust or replace sensor. | 4-5 |
| Path Monitors | | | |
| Internal Calibration Cell Defects | Errors are introduced when internal calibration cell leaks or its gas decomposes. | Check daily cal chart for jumps or drift. Replace cell. | 4-5-4-7 |
| Gas Cell Temperature Problem | Bias results if the temperature of the gas cell and flue gas differ greatly. | Correct mathematically. Install cell in "zero pipe" or outside stack in heated area. | 4-9 |
| Flow-Through Calibration Gas Availability | Protocol 1 gases often not available at required concentrations. | Use only if certified gases are available. Redesign system - use longer cell. | 4-7-4-10 |
| Transmissometers (Opacity Monitors) | | | |
| Improper System Design | Poor design produces both bias and inconsistencies with visual observations. | Redesign. | 4-10 |
| Dirty Windows | Build-up on windows produces bias. | Auto-correct. | 4-10 |
| Interferences | Water droplets and high NO ₂ distort measurements. | Calculate correction. | 4-10 |

Chapter 5 Highlights

Flow (Velocity) Monitoring System Problems

| Problem | | Corrective Actions | Page Refs |
|---|--|--|-----------|
| Name | Description | | |
| General | | | |
| Stack Area Miscalculation | Use of incorrect cross-sectional area in calculating volumetric flow can produce measurement error. | Directly measure and re-calculate. | 5-2 |
| Gas Density and Temperature Distortions | Bias can be introduced if the temperature profile is different from the velocity profile. | Verify temperature profile and use new assumptions if there is a disparity with velocity profile. | 5-2 |
| Differential Pressure Sensing Monitors | | | |
| Improper Angle of Probe Tube to Gas Flow | Measurement error can result if probe tube is not oriented perpendicular to flue gas flow. | Rectify improper orientation. Avoid using where cyclonic flow is present. | 5-3 |
| Plugging | Probe plugging can prevent accurate pressure measurements. | Increase frequency and/or pressure of blowback. | 5-3, 5-4 |
| Thermal Sensing Monitors | | | |
| Particulate Build-Up on Sensors | Particulate build-up can slow instrument response by forming an insulating layer on the probe's temperature sensors. | Remove by flash heating or blowing off deposits. Avoid by employing aerodynamic cavity design. | 5-4, 5-5 |
| Water Droplets and Acid Corrosion | Heat lost to evaporation can bias measurements. Acid droplets can eat into the metal junctions of probe arrays. | Repair and change probe design. | 5-4 |
| Ultrasonic Monitors | | | |
| Improper angle of transducers | Measurement errors can result under pitched or cyclonic flow conditions. | Orient measurement path perpendicular to the flow pitch. Where pitched flow is variable, consider using two sets of transducers in X-pattern. | 5-5, 5-6 |
| Particulate build-up on sensors. | Build-up on sensors can introduce measurement error. | Use blowers to keep transducer sensors clean. | 5-6 |

Chapter 6 Highlights

Gas Analyzer Problems

| Problem | | Corrective Actions | Page Refs |
|---|---|--|------------|
| Name | Description | | |
| General | | | |
| Interference Effects | The presence of other gas species throws off the measurement of the gas being monitored. | Change analysis technique. Measure concentration of interferent and correct for its presence. Scrub out the interfering species before analysis. | 6-2-6-5 |
| Analyzer Design | Features inherent in an analyzer's physical construction, electronic design, and analytical technique can be prone to producing measurement bias. | Choose analyzers wisely, considering bias-prone features. In QA/QC program, tailor preventative maintenance to design features that are bias prone. | 6-7 |
| Ambient Effects | | | |
| Temperature | If exposed to extreme temperatures, the analyzer may produce erroneous readings. | Temperature stabilize the analyzer. Measure temperature and compensate. | 6-5, 6-6 |
| Pressure | Changes in barometric pressure can introduce systematic error in spectroscopic systems where measurements are made from a sample cell. | Monitor pressure and mathematically compensate for pressure effects. | 6-6, 6-7 |
| Polluted/ Corrosive Atmosphere | Situations like plume downwash or flue gas exhausting into CEM shelter can produce systematic error or system failure. | Shelter or otherwise protect system. Filter ambient air. | 6-6 |
| Calibration | | | |
| Incorrect Gas Values | If the presumed and actual calibration gas concentrations differ significantly, biased measurements will result. | Replace or recertify gas. Find actual concentration. Recalculate effluent concentrations. | 6-8 |
| Inadequate/ Inconsistent Response Time | Bias can develop if operator or operating system does not allow adequate time for monitor to reach its asymptotic value. | Establish procedures that ensure consistently adequate time for monitor response. | 6-9-6-11 |
| System Calibration Obscuring Local Bias | Routine analyzer adjustments during full system calibration can mask local sources of bias. | Perform probe and local analyzer calibration checks in addition to system checks. | 6-11, 6-12 |

Chapter 7 Highlights

Data Acquisition and Handling System (DAHS) Problems

| Problem | | Corrective Actions | Page Refs |
|--|--|--|-----------|
| Name | Description | | |
| Improper Interfacing | | | |
| Distorted Inputs from Analyzer | Input signals to the DAHS from the analyzer, process controller, or sensors are distorted. | To detect problem, compare DAHS readings to strip chart recorder's. Replace or repair faulty components. | 7-2 |
| Synchronization Problems | Errors will result if system control and DAHS clocks are out of synchronization. | Prior to certification testing, fix any mismatch between system and DAHS clocks. | 7-2, 7-3 |
| Calculation Problems | | | |
| Round-Off Problems | Incorrect rounding methods can produce biased results. | Change math to meet accepted professional practices and the conventions in regulations. | 7-3 |
| Incorrect Parameters | Entering incorrect values for user-configurable parameters will produce recurring errors. | Re-enter correct values. | 7-4 |
| Incorrect Equations | Programming incorrect equations will produce recurring calculation errors. | Require DAHS developers to document and validate all equations and correct code. | 7-4 |
| Improper Correction Routines | | | |
| Automated Zero/Span "Corrections" | Such adjustments may not be warranted and, at times, can introduce errors. | Do not allow automated corrections, OR Require vendor to precisely define and print out each adjustment. Include definitions in QC plan. | 7-5, 7-6 |
| Flow Monitor Correction Factors | If not correlated with actual conditions, these factors can produce systematic error. | Re-test under all prevailing conditions. Then, re-calculate the factors. | 7-6, 7-7 |
| Faulty Dilution System P/T Corrections | Pressure and temperature corrections can produce errors if incorrectly derived. | Require vendor to specify factors used and how derived. Correct if wrong. | 7-7 |
| Bias Adjustment Factor (BAF) | The BAF is a regulatory remedy, not a technical correction for systematic error. | Avoid having to apply a BAF by eliminating the sources of bias. The lower the BAF, the higher the confidence in the CEM's accuracy. | 7-7, 7-8 |