## **CHAPTER 3**

# SOURCES OF BIAS IN EXTRACTIVE CEM SYSTEMS

## **Chapter 3 Highlights**

### **Sampling System Problems — Extractive CEMS**

	Problem	Corrective	
Name	Description	Actions	Page Refs
Probe Proble	ms — Source Level Systems		
Plugging	Particulate matter clogs sampling probe.	Blowback. Increase filter surface area.	3-3, 3-4
Scrubbing	Precipitates on probe "scrub" $\mathrm{SO}_2$ from sample gas.	Blowback. Redesign.	3-3, 3-4
<b>Probe Proble</b>	ms — Dilution Extractive Syst	ems	
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.	3-5, 3-6
	Ü	Add probe heater. Replace with ex-situ probe.	
Droplet Scrubbing	Evaporation of droplets in sonic probe can plug probe or cause prediluting 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 Sampl	ing 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 <sub>2</sub> 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

#### **Source-Level Extractive**

- C Hot-wet
- Cool-dry
  - Conditioning at probe
  - Conditioning at shelter

#### **Dilution-Extractive**

- C In-stack dilution probes
- C 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:

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

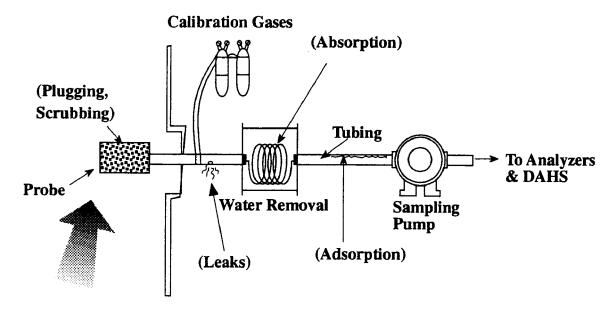


Figure 3-1. Potential Sources of Bias in Extractive Systems

#### 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  $SO_2$  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  $SO_2$  concentration would not decrease appreciably. Corrective action involves extracting, disassembling, and cleaning the probe and probe filter immediately after the upset.

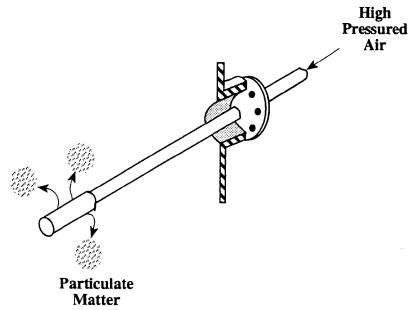


Figure 3-2. Probe Blowback

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  $SO_2$  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 lead 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.  $H_2O$  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.  $H_2O/percent$  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.,  $SO_2$  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  $SO_2$ , NO, and  $CO_2$  where the  $CO_2$  concentration may be 20% of the total gas composition.

<sup>\*</sup> The findings discussed here are based on laboratory and field tests of the EPM probe.

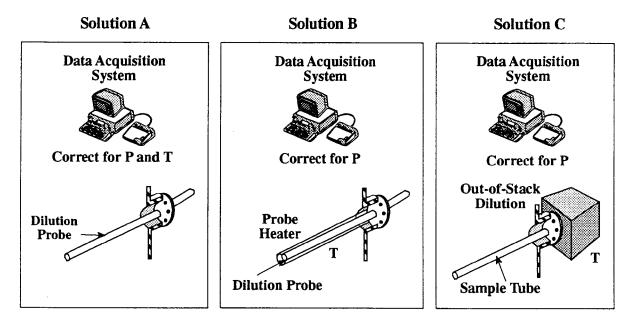


Figure 3-3. Solutions to Dilution System Bias Problems

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  $\mathrm{CO}_2$  at a concentration close to that contained in the flue gas. However, this solution is problematic when the regulations specify using a  $\mathrm{CO}_2$  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  $\mathrm{CO}_2$  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  $\mathrm{CO}_2$ . 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 <sub>2</sub> in nitrogen)	Emission measurements are biased (because ${\rm CO_2}$ present in flue gas).
Calibration Error Test and Linearity Check	CEM system calibrated with single blend	Calibration error test conducted with CO <sub>2</sub> triple blend will show a bias. Linearity check conducted with CO <sub>2</sub> 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.
	CEM system calibrated with single blend.	RATA conducted with Reference Method 6C calibrated with a CO <sub>2</sub> triple blend will show bias.
	CEM system calibrated with CO <sub>2</sub> triple blend.	RATA conducted with Reference Method 6C calibrated with a single blend will show bias.
RATA	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 $\mathrm{CO}_2$ 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  ${\rm CO_2}$  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

- Use CO<sub>2</sub> 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,  $CO_2$ , 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 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  $SO_2$  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.  $O_2$   $CO_2$ , and CO do not commonly adsorb on most sample line materials. NO, SQ, and  $NO_2$  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.

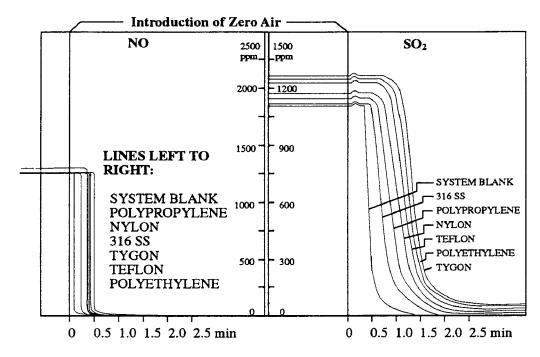


Figure 3–4. Desorption Times of NO and SO<sub>2</sub> with Various Clean Sample Line Materials at a Length of 15.2 m (McNulty, 1974)

#### 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  $SO_2$  at concentrations on the order of 100–1,000 ppm that, under a variety of conditions, from 3–15% of the  $SO_2$  could be lost in the chiller. The work also projects that at  $SO_2$  levels of 10 ppm at 20% moisture, losses can be on the order of 30%. Freitag's general observations follow:

"The fraction of SO<sub>2</sub> removed from the analysis by a refrigerated trap:

- (1) increases with increasing moisture content of the stack gas,
- (2) increases with decreasing SO<sub>2</sub> content, and
- (3) increases with decreasing trap temperature."

These losses can be calculated if the stack gas dewpoint, sample gas flow rate, wet basis  $SO_2$  level,  $SO_2$  solubility, and condenser temperature are known.

Gasabsorptionmay 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  $SO_2$  solubility, (c) acidifying the gas stream with an unmonitored acid to reduce  $SO_2$  solubility (DeFriez, 1992), and (d) using some other method of moisture removal such as Nafion<sup>TM</sup> 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  $SO_2$  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  $\rm O_2$  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  $\rm O_2$  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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#### 3.10 ADDITIONAL READING

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Myers, R.L. 1986. Field Experiences Using Dilution Probe Techniques for Continuous Source Emission Monitoring. Transactions - Continuous Emission Monitoring - Advances and Issues. Air Poll. Control Assoc., pp. 431-439.