

Chapter 9

Emission Measurement, Monitoring & Reporting

Editor's Note:

Chapter 9 – Emissions Measurement and Reporting - is most of Chapter 13 from the 2000 version of APTI 418 written by James A. Jahnke. Brian Doyle provided some of the final section on Emission Calculations

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OVERVIEW

Continuous emission monitoring (CEM) provides real-time immediate indication of emissions. As discussed in earlier chapters, NO and NO₂ are formed simultaneously in combustion processes and other high temperature operations. NO typically represents 90% to 95% of NO_x for sources with emissions higher than about 25 ppm. NO is insoluble while NO₂ is moderately soluble. Moisture in the flue gas can be removed with only a slight loss of NO_x because NO₂ represents a minor portion of the total NO_x in a sampled stream and well designed condensers minimize the contact between gas and liquid water. The ability to remove moisture from the sample gas prior to measurement opens many CEM system configuration options.

NO_x is determined with an assortment of measurement techniques. NO absorbs light in portions of the ultraviolet (UV), visible, and infrared (IR) spectra bands. These absorbent bands allow for a variety of spectroscopy measurement techniques. Another measurement technique is based on the principle of chemiluminescence resulting from NO and ozone interaction.

Continuous monitoring techniques are also used for measuring ammonia. These systems are relatively similar to those for measuring NO_x, except that some newer techniques have recently (2001) developed for ammonia.

Typical CEM systems are comprised of analyzers, a data acquisition system, a sample acquisition and conditioning system, and calibration equipment. They typically include a system for injecting calibration gases for daily calibration and quarterly audits.

CEM REGULATORY PROGRAM

Regulations and monitoring are interrelated. Regulatory requirements dictate the types of CEM systems that are to be installed and the manner in which they are to be operated. Alternatively, the advancement and development of monitoring technologies can result in regulations specifying the use of such technologies.

CEM regulatory programs have three distinct phases. The first is the *implementation*. This includes the regulations that require certain source categories to install CEM systems. The next phase is *certification* where the source must demonstrate that the CEM system operates in a concise and accurate manner. EPA, the International Standards Organization (ISO) and the American Society for Testing Materials (ASTM) have standards for conducting such certifications. Finally, after the CEM system is installed and certified, it must operate for long periods of time. The typical lifetime of a CEM system can be five to ten years, depending on the type of system and how well it is maintained. If a quality assurance plan is implemented, the CEM system can provide data availability for 95% to 99% of the time.

Implementing Rules

The regulations or rules that require the installation and use of CEM systems can be either federal or state/local. The first programs to be established were the Federal New Source Performance Standards (NSPS) that are codified in 40 CFR Part 60. However, state and local agencies can also require CEMs through their permit programs.

Through the NSPS program, EPA requires permanently installed CEM systems for NO_x monitoring at fossil fuel-fired steam generators, electric utilities, industrial and commercial steam generating units, municipal waste combustion, and nitric acid plants. More recently, the acid rain program in 40 CFR Parts 75 and 76 has required that NO_x be continuously monitored as part of the emissions trading program.

State/local air agencies are mandated by various federal programs to require sources to install (or allow as an option to install) a CEM system. Some examples include the Prevention of Significant Deterioration (PSD) and the Compliance Assurance Monitoring (CAM) programs. Another state/local program that requires NO_x monitoring is the RECLAIM program in California, which is similar to the Acid Rain Program, but on a regional level instead of a national level.

Other discretionary programs such as variances, orders and court-ordered agreements can require the installation of a CEM system.

MEASUREMENT TECHNIQUES

NO_x Measurement Techniques

Many commercial CEM NO_x analyzers, based on a variety of measurement techniques, are available. Most are based on optical absorption governed by the equation:

$$Tr = \frac{I}{I_0} = e^{-\alpha(\lambda)cl}$$

Equation 9-1

Where:

Tr = transmittance of light through the flue gas

I₀ = intensity of the light entering the gas per unit time

I = intensity of the light leaving the flue gas per unit time

α(λ) = molecular absorption coefficient

c = pollutant concentration

l = path length of light

Methods of NO_x measurement are chemiluminescence, infrared spectroscopy, ultraviolet spectroscopy, and electrochemical cells.

The common types of monitors presently used for nitrogen oxides determination with *extractive* systems use the following techniques:

- Chemiluminescence (NO_x)
- NDIR spectroscopy (NO)
- Gas filter correlation spectroscopy (NO)
- Nondispersive ultraviolet spectroscopy (NO_x)
- Polarography (NO_x)

In-situ monitors use the following methods:

- Gas filter correlation spectroscopy (NO)
- Differential absorption spectroscopy (NO)
 - ◇ Using diffraction grating
 - ◇ Using diode array detectors
- Diode array detectors (NO)
- Polarography (NO).

Two types of extractive systems are the most commonly used. Extractive and in-situ CEM systems are discussed later in this chapter.

Chemiluminescence

Chemiluminescence analyzers are the most common type of NOX emission monitors presently applied to CEM systems. The principle of chemiluminescence involves the reaction of NO and instrument-generated ozone as shown in Figure 9-1.

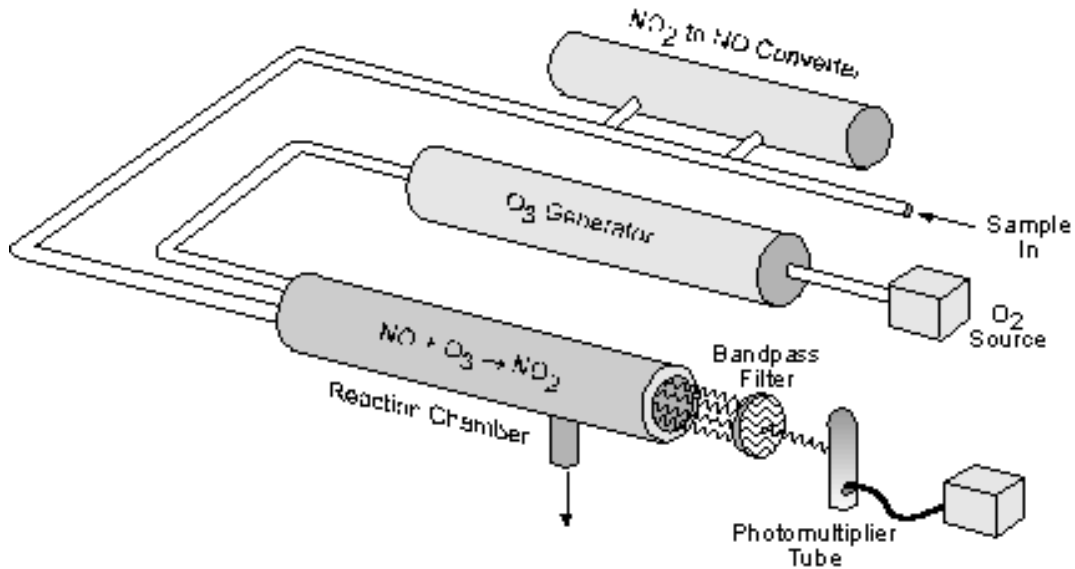


Figure 9- 1. Chemiluminescent methodology

Before analysis, sampled gas is directed through a thermal converter to reduce any NO₂ to NO. The gas sample is then blended with instrument-generated ozone in a reaction chamber where the NO is converted to electronically excited NO₂ molecules, as shown in Reaction 9-1.



The excited NO₂ molecules quickly release their excess energy by emitting a photon as they drop to a lower energy level (Reaction 9-2). The photons, or light emissions, are directly proportion to the NO concentration in the sampled gas. The light emissions for a narrow wavelength corresponding to the reaction are monitored by a photomultiplier tube.



Ammonia can also be measured with this technique by first converting the ammonia to NO in a converter and then measuring the NO in the analyzer.

Spectroscopic Techniques

Since NO_x absorbs both IR and UV light, spectroscopic techniques can use either region of the spectrum. These techniques include: differential absorption spectroscopy; gas filter correlation spectroscopy; Fourier transform infrared (FTIR) spectroscopy; and second derivative spectroscopy. Of these four methods, all but FTIR spectroscopy can be used in either extractive or in-situ systems. FTIR spectroscopy can only be used in extractive systems.

Differential Optical Absorption Techniques

The basic technique of differential optical absorption includes a radiation source emitting light that is transmitted through the sample and then measured by a detector. A detector measures the wavelength of light in the absorption band of the pollutant gas (i.e., NO_x) and a wavelength not absorbed by the pollutant gas. The Beer-Lambert Law states that the difference of the energy of the wavelengths is related to the gas concentration. The differential optical absorption technique is employed for extraction and in-situ systems.

The following section describes several specific differential optical absorption designs that are commercially available.

Optical Filters - Two optical filters are mounted near the light source. One filters light except for a wavelength, λ_0 , not absorbed by NO_x molecules. The second filter allows only light of a wavelength specific to NO_x , λ_1 , to pass into the gas cell. A detector measures both wavelengths of light after they pass through the gas cell (Figure 9-2).

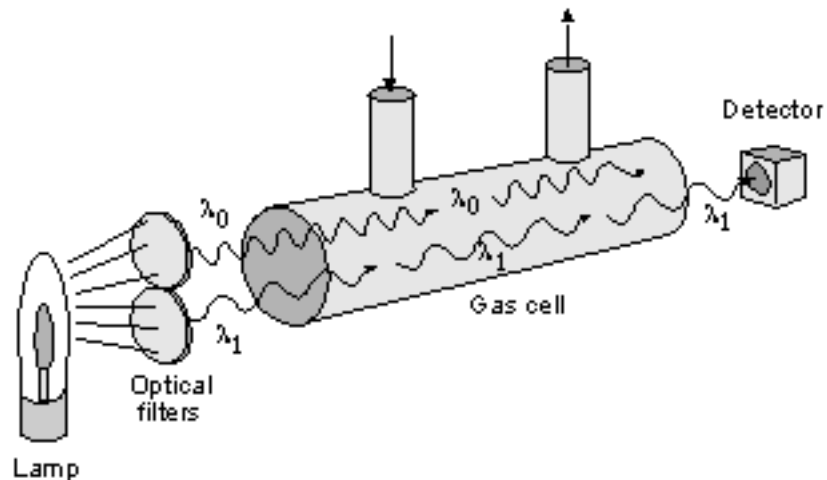


Figure 9- 2. Differential optical absorption using optical filters

Moving Slit - All of the light from a source passes through the gas sample and is reflected to a rotary disk containing two slits. One slit allows light of a wavelength not specific to the pollutant gas, λ_0 , to reach the detector. The other slit allows light specific to the pollutant, λ_1 , to reach the detector. As the disk rotates, the detector measures the alternating λ_0 and λ_1 signals (Figure 9-3).

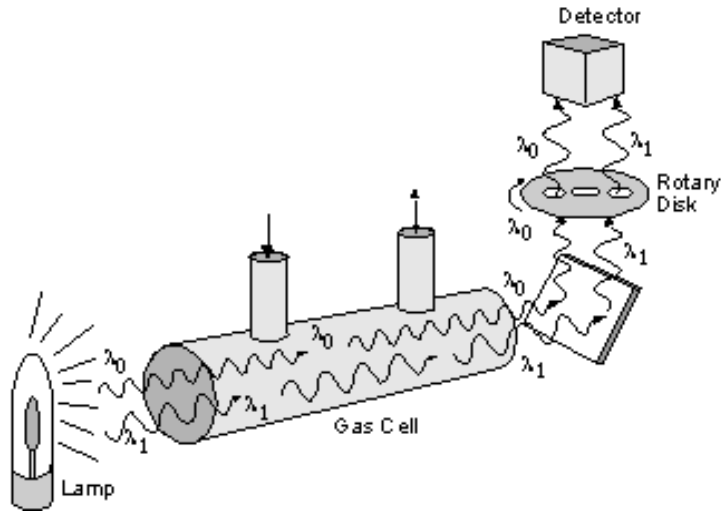


Figure 9- 3. Differential optical absorption using a moving slit

Diode Array Detector - A diode array detector, shown in Figure 9-4, is a common design for in-situ systems. All of the light from a source passes through the gas sample. The light wavelengths λ_0 and λ_1 are separated by a diffraction grating, and a diode array detector measures the amount of energy for the two wavelengths.

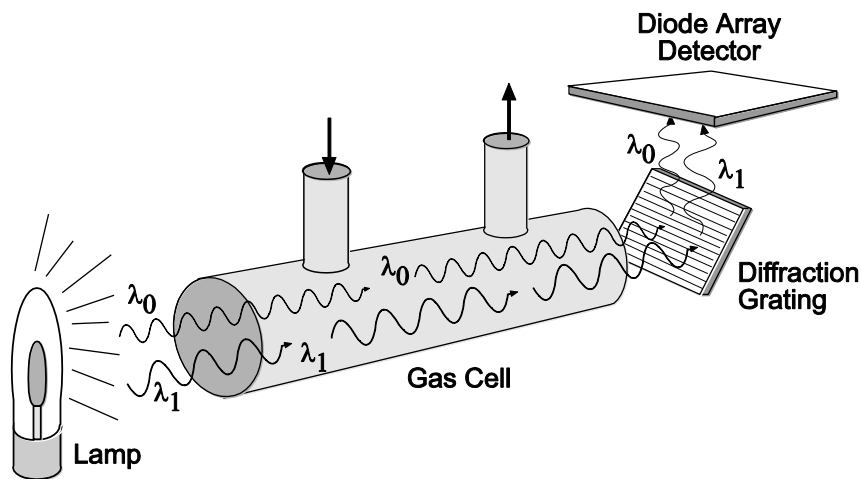


Figure 9- 4. Differential optical absorption using a diode array detector

Diode Laser - A diode laser, shown in Figure 9-5, is a recent design. The light source is a diode laser that emits light of wavelengths λ_0 and λ_1 . The light passes through the gas sample and is measured by a detector.

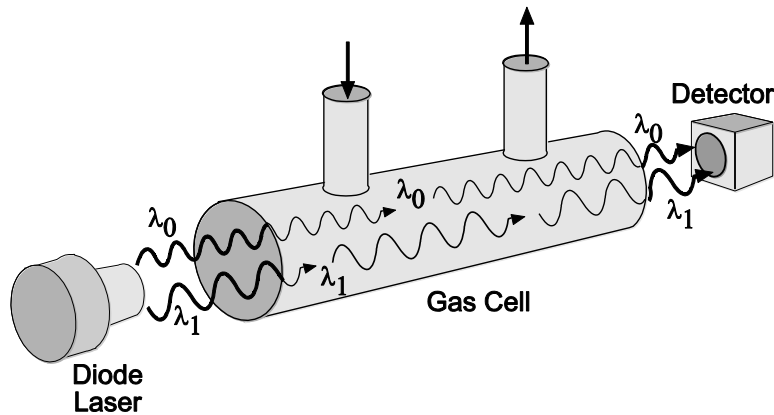


Figure 9- 5. Differential optical absorption using a diode laser

Gas Filter Correlation (GFC) - GFC is applied not only to NO measurement, but also to measurement of CO₂, CO, NH₃, H₂O, HCl, SO₂ and hydrocarbons. GFC is applied to both extractive and in-situ monitors. A GFC design is shown in Figure 9-6.

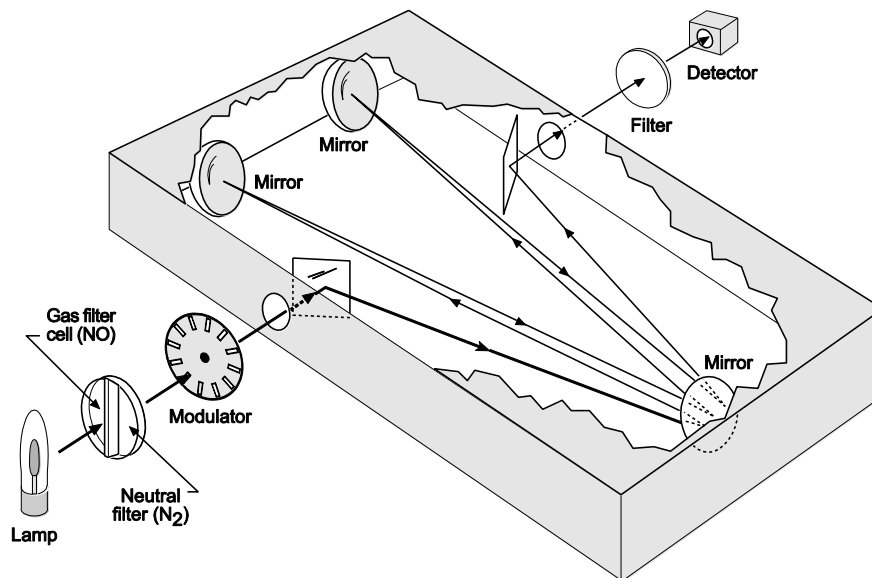


Figure 9- 6. Gas filter correlation design

GFC differs from other NDIR spectroscopy in that all of the reference signal energy is absorbed for the target gas compound. The infrared light emitted from a source passes through a rotating filter wheel. Half of the filter contains a neutral gas that allows the light of interest to pass through. The other half of the filter contains the target gas, which absorbs nearly all of the light at the wavelength specific to the target pollutant. After exiting the filter wheel, the light passes through a modulator to

create an alternating signal. The alternating signal then enters the sample cell where it reflects through a series of mirrors to increase the path length and improve the sensitivity of the instrument. The difference of the alternated light signals is measured to provide the gas concentration.

Polarographic Techniques

Polarographic instruments (electrochemical transducers) utilize a transducer to measure the voltage drop produced from a chemical reaction involving the target pollutant. A chemical reaction current takes place in an electrochemical cell where a selective semi-permeable membrane causes the pollutant to diffuse to an electrolytic solution. The change in current is then measured as the oxidation or reduction reaction takes place.

Ammonia Measurement Techniques

Ammonia monitoring methods include: chemiluminescence, IR spectroscopy, UV spectroscopy, electrochemical methods, and ion-mobility spectroscopy. One of the chief difficulties for extractive systems that monitor ammonia is the loss of ammonia in the sample lines. Ammonia is extremely soluble in any condensed water.

CEM SYSTEMS

CEM systems are categorized in terms of the specific components and sampling techniques. Types of CEM methods include *extractive*, *in-situ*, *parametric*, and *remote sensing*. Source operating parameter monitoring is sometimes used as an alternative to an instrument-based monitoring system. *Extractive systems* are most commonly employed. Extractive systems remove a portion of the flue gas from the stack or duct for measurement of emissions.

An extractive CEM system consists of a sampling interface system, gas analyzer(s), and data acquisition/controller system. The *sample interface* system comprises all components that transport and condition the sampled gas.

One problem with extractive systems is the potential for gas loss in the system components. An option for minimizing the potential for these gas losses is the *in-situ* monitoring method. *In-situ* monitoring eliminates the need for sampling interface equipment, because they measure emissions without removing or modifying the flue gas. Measurement is made with a light source or electrochemical system (discussed in Section 9.2).

Remote sensing and *parameter* monitoring can eliminate the need for installed CEM systems. In parametric monitoring a parameter such as temperature, pressure drop, or fuel flow is correlated with emissions data based on a source test. The emissions data is correlated with the parametric values, using models such as a *least squares* model. This allows a program to be developed that can predict emissions based on the correlation and monitoring of the parametric values. Each system has

unique advantages and disadvantages. The most appropriate CEM system is dependent on the site-specific application and regulatory requirements.

Overview of Systems

Extractive Systems

The sample interface system can either introduce gas to the analyzer(s) in flue gas concentrations (*source level* systems) or in a diluted form (*dilution* systems). The source level system can be either *wet* or *dry*. Depending on the specific requirements of the gas analyzer, the sample gas is introduced as either wet or dry. Water is removed from the gas sample to provide a dry sample, and removed to a lesser extent in a wet sample.

The concentration levels of the flue gas must be within the range of the gas analyzer for source level systems. Stack gas constituents, such as particulate matter or water vapor, will cause sampling or measurement problems if not removed. Water interferes with readings for certain measurement techniques and must be removed upstream of the analyzer.

Particulate matter can lead to solids buildup and plug sampling interface components or the analyzer itself. All extractive CEM systems remove particulate matter prior to measurement. If water vapor is allowed to condense on the particulate matter prior to filtering, an agglomerated material may form. Particulate matter is often removed in the sampling probe to prevent water condensation. Filtering is usually accomplished with a sintered stainless steel or ceramic filter. Filters located in the stack or duct are typically shielded from the direct flow of the flue gas stream, which prevents coarse or super coarse particulate matter from contacting the filter.

In the dilution system, the flue gas is typically diluted to a ratio 100:1 to 300:1. The sample can then be analyzed in an ambient air analyzer that is sensitive in the parts-per-billion (ppb) range. Dilution systems can be either in-stack or out-of-stack.

In-Situ Systems

In-situ systems are either *path-type* systems or *point-type* systems. In path-type systems, a beam of light is transmitted across the stack to a detector. These systems can be either *single-pass* or *double-pass*. In a single pass system the light is beamed across the stack to the detector. In a double pass system the light is beamed to a reflector that sends the beam back across the stack to the transceiver.

In point-type systems, the measurement is made within the stack over an area of about five to twelve or more inches. The measurement can be made using a light, electrochemical, or electrocatalytical sensor. The advantage of the point monitoring system is that calibration gases are readily available for daily span, zero checks, and quarterly cylinder gas audits.

Parametric Systems

There are two types of parametric monitoring methods: using *parameter surrogates* or *predictive* methods. Parameter surrogate systems do not use a lb/MMBtu or lb/hr emission limit to determine compliance, but rather a parameter (such as pressure drop across the scrubber bed) that is indicative of compliance with the emission limit. Predictive monitoring involves the use of a range of parameters that are input into a model to predict emissions. This approach can use either theory-based models or empirical models.

Extractive CEM Systems

Cool-Dry Systems

Cool-dry systems are the most typical extractive systems.

For a source-level cool-dry extractive CEM system, the water vapor and particulate matter are removed prior to measurement, and readings are taken on a *dry basis*. Although the configuration differs slightly from system to system, the sampling interface generally consists of a probe, filter, conditioning system, and pump.

Figure 9-7 shows an example of a cool-dry extractive system with the conditioning system located near the analyzer. This configuration requires a heated sample line, which allows for greater accessibility to the conditioning system. A pump is used to continuously extract flue gas from the stack at a constant flow rate by. The flue gas enters a probe situated at an appropriate location inside the stack, passes through a filter, and remains heated until it reaches the conditioning system. The conditioning system, consisting of either a condensation device or permeation tubes, removes the moisture and reduces the temperature of the sample prior to analysis. It is critical to extract the water, because many analyzers have been designed for dry gases and because, as previously discussed, water can be an interferent.

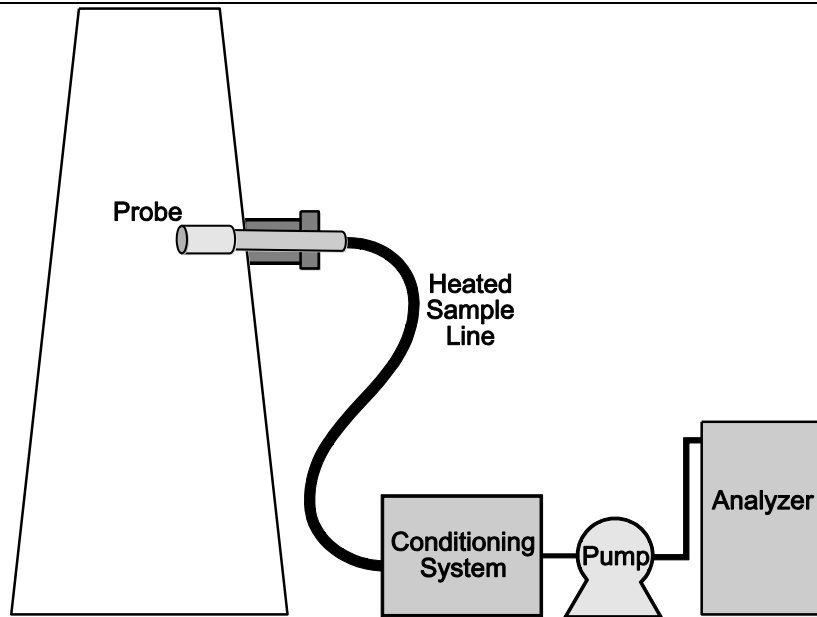


Figure 9- 7. Cool-dry extractive system with conditioner

The condenser can be a mechanical refrigerator, an electric refrigerator, or a thermoelectric cooler. Either of these devices keeps the temperature of the gas below the dew point and above the freezing point of water. As liquid collects in the condenser, it must be manually or, preferably, automatically drained. Water contact with the sample gas should always be kept at a minimum to reduce NO_2 loss.

Permeation tubes contain an ion exchange membrane to remove condensed liquid from the gas. Permeation tubes prevent gas-liquid contact; however, they may be susceptible to plugging. It is beneficial to locate the conditioning system upstream of the sampling pump. This will prevent water or acid gas condensation in the pump and lengthen its operating life.

The cool, dry, particulate-free sample is transported to the gas analyzer(s) for measurement. The analyzer conveys analog or digital output signals to a DAS. Gas cylinders with known gas concentrations are often used during calibration to prove the CEM system is devoid of leaks and the DAS is recording accurate values.

Calibrations for almost all NO_x monitoring require the use of EPA Protocol 1 gases. These gases are certified the strict procedures outlined in the EPA document entitled *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors: Protocol 1*. EPA Protocol gases are within 1% of National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs).

NO and N_2 blends of gases are required for calibrations. Degradation of blended NO_x EPA Protocol 1 gases will occur over time. The certification period for NO/N_2 blends in aluminum cylinders is 18 months (≥ 10 ppm) from the last analysis. Therefore, special attention should be given to the expiration date of calibration gases.

Because NO is a mildly corrosive gas, all metal components in contact with it must be corrosion resistant. Regulators should be of stainless steel material to minimize air diffusion and adsorption, desorption, and off-gassing.

RM testing is typically performed using a cold-dry extractive system. Infrared-based analyzers measure on a dry basis because water vapor absorbs light throughout most of the infrared spectrum. These systems are simple in their design. Maintenance of the system consists of maintaining the heated sample lines and the plumbing to avoid leaks and corrosion problems.

Figure 9-8 shows another type of extractive system where the sampled gas is conditioned immediately upon exiting the stack or duct, making a heated line unnecessary. The conditioning system for this kind of arrangement is often less accessible for inspection and repairs. This type of system is not typically installed in the field, but more likely to be used by a source testing company.

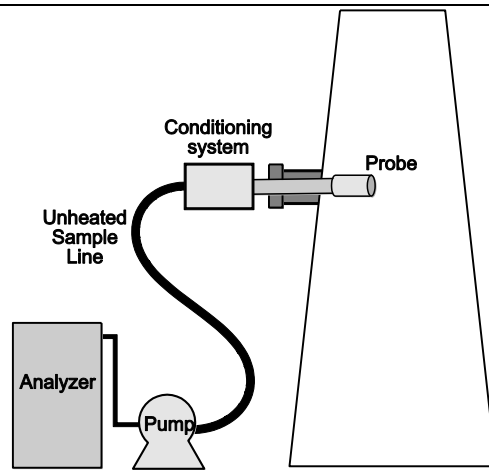


Figure 9- 8. Cool-dry extractive system without conditioner

Hot-Wet Systems

Hot-wet extraction systems send the sample gas to the analyzer(s) without removal of water vapor (Figure 9-9). All components of the sample acquisition system that contact the sample must be sufficiently heated ($248^{\circ}\text{F} \pm 25^{\circ}\text{F}$) to prevent condensation of water or acid gases. The heated components require routine inspection and maintenance. Components of hot-wet systems may have to be replaced periodically because heated components tend to degrade faster than unheated components.

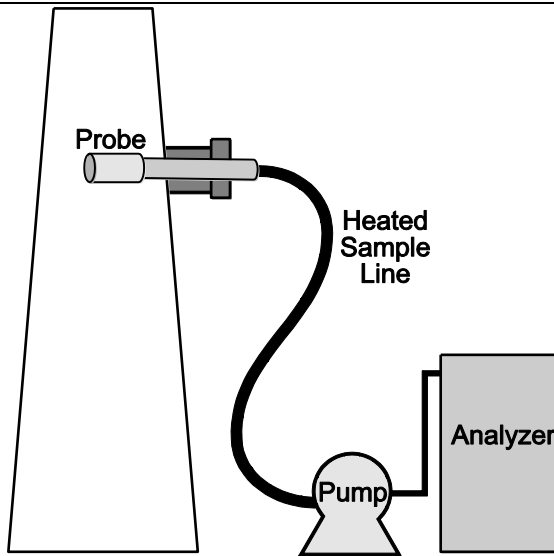


Figure 9- 9. Hot-wet extractive system

Ammonia is an example of a gas that must be measured in a hot-wet manner. Ammonia will be absorbed in condensed water if the sample temperature is lowered to remove the water vapor.

Dilution Systems

The main disadvantage of source-level systems is the continual conditioning of a large volume of stack gas required. However, dilution systems require much less conditioning by sampling flue gas at a low flow rate. Flue gas is diluted either inside or outside the stack or duct. Dilution systems send either wet or dry gas containing low pollutant concentrations to the analyzer(s). However, it is often not necessary to remove water vapor because of the high dilution ratios. The analyzers generally used for these concentration levels are ambient air monitors, which are designed for lower concentrations.

In-Stack Dilution – This system consists of a dilution probe situated inside the stack. Clean, dry air is sent to the probe at a specific rate and a critical orifice usually controls the source-level sample gas. The use of the critical orifice with clean, dry air brings the temperature of the sample below the dew point so that it can be measured on a dry basis in the analyzer. Dew points of -40°F are typical. Dilution ratios are selected to accommodate the temperature. Dilution ratios of 50:1 to 300:1 are generally achieved.¹ A dilution probe is shown in Figure 9-10.

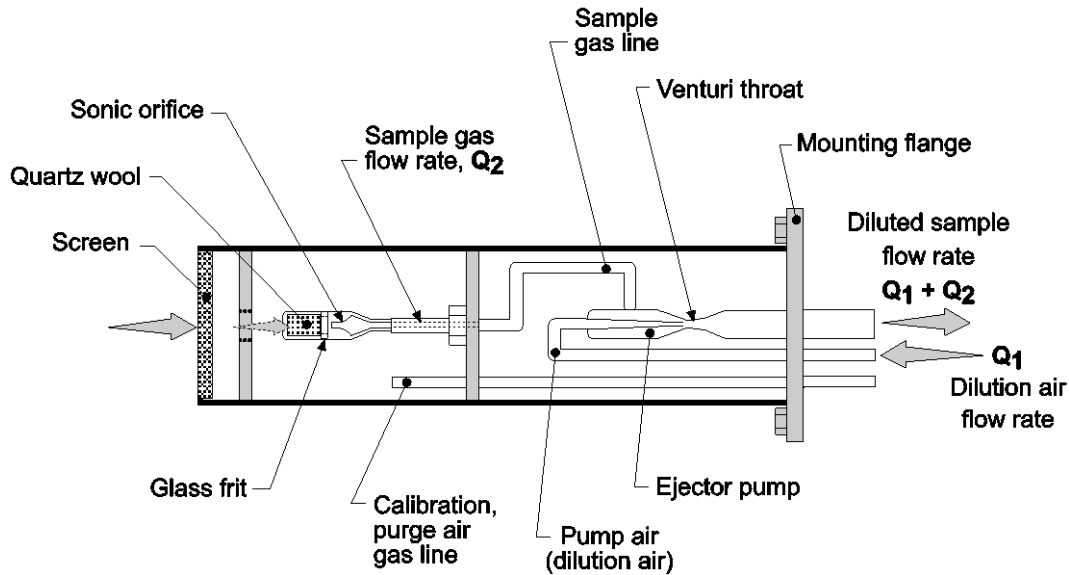


Figure 9- 10. In-stack dilution probe

One advantage of this system is that there is no need to remove the water from the sample prior to analyzing the gas. As a result, this system could be used with an ammonia analyzer that is sensitive enough to use with a dilution system. On the other hand, the in-stack dilution system does not work well with stack gas containing wet, sticky particulate matter or entrained water droplets that can plug the glass frit or orifice. Out-of-stack dilution systems can provide a more accessible system for servicing.

Out-of-Stack Dilution – This system dilutes the sampled gas outside the stack or duct. Flue gas is diluted with a dilution orifice near the sampling location, at the CEM shelter, or at a location in between. A heated sample line may be used from the sampling location to the dilution assembly depending on the proximity of the dilution system to the sample probe. The dilution assembly should be located at an easily assessable location and it can be heated with a jacket to minimize condensation problems. Condensed acid gases such as sulfuric acid may corrode components of the dilution assembly. Water condensation can absorb soluble gases and create flow problems. Out-of-stack systems have an advantage over in-stack systems, because a slipstream can be drawn from the heated sample line for oxygen determination. After dilution, the oxygen levels are too close to ambient levels to allow accurate readings.

The disadvantages of the out-of-stack dilution system include the added expense, maintenance, and inspection required for the heated components of the sample interface system. In addition, the response time for out-of-stack dilutions systems is slow because of the low flow rate of the sample through the sample line. However, the conditioning of only a small gas flow is attractive to many facilities.

Close-Coupled System

The close-coupled system is an extractive CEM design in which the gas analyzer is installed at the gas sampling location. They consist of a sample probe with a pump to transport the sample to the analyzer. A close-coupled CEM system eliminates the sampling line from the sampling interface for extractive source-level systems. The removal of the sample line minimizes problems caused by reactive, condensing, or adsorbing gases. A disadvantage of the close-coupled system is the location of the analyzer. The analyzer can be more susceptible to environmental factors and is less accessible for inspection or repair.

In-Situ CEM Systems

In-situ CEM systems measure flue gas components in the stack without altering or removing flue gas. Path or point in-situ sampling systems measure the flue gas either by using a light source or by an electrochemical technique.

Point Systems

Point systems consist of a transceiver and probe. The transceiver sends light to a retroreflector in the probe that reflects the light back to the detector. Point systems measure the flue gas at a point or a path that is short, relative to the stack diameter (path lengths can reach 1-1½ feet in length depending on the type of instrument). Common point systems techniques for NO_x analysis include differential absorption, gas filter correlation infrared, second derivative ultraviolet spectrometers, and electrochemical. An example of an infrared in-situ point monitor is shown in Fig 9-11.

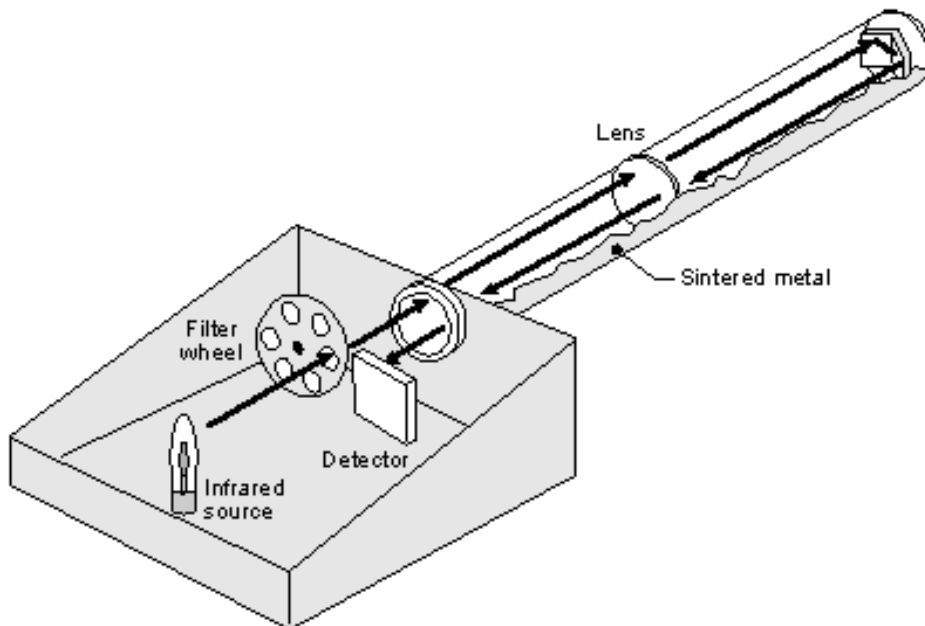


Figure 9- 11. Procal UV differential absorption point in-situ monitor

Point systems can use calibration gas to calibrate the instrument by flushing flue gas out of the sensing chamber at the end of the sample probe.

Point systems are easier to calibrate than path systems because the sampling area can be flooded with calibration gas. There are no pumps or gas conditioning system associated with these types of systems.

Point systems are susceptible to environmental factors. Problems associated with environmental factors include (1) misalignment of components, (2) loosening of circuit boards and other electrical equipment, (3) cracking of components, and (4) corrosion of components. Heavy particulate matter loading or water droplets may clog the sintered or ceramic filter protecting the sample probe. Fine particulate matter may penetrate the filter.

If the flue gas is stratified within the stack or duct point, in-situ monitoring will not provide an accurate representation of the entire flue gas stream. In-situ monitoring systems generally require less inspection and maintenance relative to extractive CEM systems. However unlike in-situ systems, analyzers and components of the extractive system can be located in a more accessible, controlled, and protective environment.

Path Systems

Path in-situ systems use optical instruments to measure the analyte across the approximate equivalent diameter of the stack or duct. A light source sends light across the path length, and a detector measures the light after it has passed through the flue gas. Path in-situ monitoring can be accomplished with one or two passes of the light across the flue gas.

The principal measurement techniques for path in-situ CEM systems are differential absorption spectroscopy, second derivative spectroscopy, and gas filter correlation spectroscopy.

The transmitter and the detector are located on opposite sides of the flue gas stream in single-pass systems. A double-pass system uses a retroreflector to transmit the light across the stack or duct a second time. Single-pass and double-pass in-situ monitors are shown in Figure 9-12 and Figure 9-13, respectively.

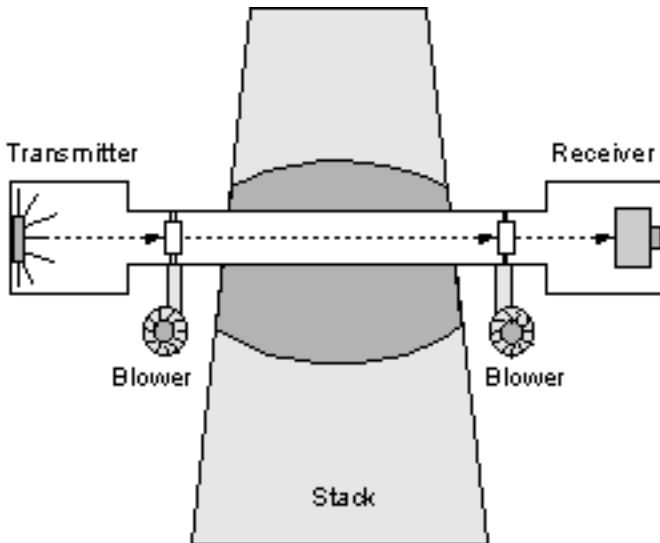


Figure 9-12. Single-pass in situ system

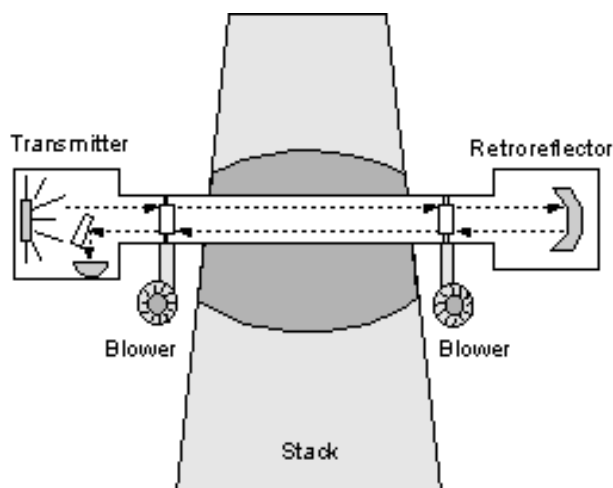


Figure 9-13. Double-pass in situ system

Path systems are advantageous for stratified sources because they sample across the entire stack or duct. In addition, problems associated with sample acquisition equipment are eliminated with path systems.

In-situ path CEM systems must be able to withstand environmental factors (e.g., weather, vibration, and temperature). The alignment of the optical components can be altered and

must be checked periodically. High opacity in the flue gas caused by particulate matter or water droplets can result in low transmittance of light to the detector.

There are various methods for calibrating these systems, including checking the calibration without the use of calibration gases. Calibrations or audits with calibration gas are difficult for single-pass path systems.

Remote Sensing CEM Systems

Remote sensing is performed by projecting light through the plume or sensing light radiation of flue gas molecules. Remote sensing CEM systems eliminate the sample interface equipment required by extractive monitoring. Aside from opacity monitoring, commercialization of remote sensing has been limited.

Parametric Emission Monitoring

Parameter monitoring uses indirect inputs to predict flue gas emissions, and can indicate the possibility that a facility is out of compliance with EPA regulatory requirements.

Parameter inputs are used as parameter surrogates, or they can be integrated into predictive emission monitoring systems (PEMS). These inputs include temperature readings, pressure readings and fuel input data. The Compliance Assurance Monitoring (CAM) program promotes the use of parametric monitoring.

Parameter Surrogates

Parameter surrogates are monitored to observe the performance of air pollution control devices. A variation from the operating baseline values often indicates an increase in emissions. Operating permits may stipulate limits on control equipment

during operation if emissions are not measured directly. Some of the surrogate indicators for SCR and SNCR systems are provided in the following sections.

SCR and SNCR Reagent Feed Rates and Injection Conditions - The feed rates of anhydrous ammonia (gas), aqueous ammonia (liquid), and urea (liquid) are monitored by conventional liquid or gas flow rate monitors. The feed rate should be recorded and compared with the design values for the operating rate of the combustion system. Low values indicate that the stoichiometric ratio between the reducing agent (e.g., ammonia) and the NO_x is too low; therefore, the NO_x concentrations in the stack could be high. High values indicate that excessive quantities of the reducing agent are being added, and there may be excessive “slip” emissions.

Proper distribution of the reducing agent (e.g., aqueous ammonia) is very important. This is partially dependent on the pressures in the supply headers feeding the nozzles. It is also dependent on the flow rates of the carrier streams such as preheated air for anhydrous ammonia and water for aqueous ammonia. These data should also be monitored and recorded to help operators routinely evaluate the performance of the NO_x control system.

Gas Temperatures - Both the SCR and SNCR systems have limited gas temperature operating ranges. In SCR systems, the gas temperatures at the inlet to the catalyst bed should be monitored. This data can be compared against the required temperature range for the type of catalyst being used. Low gas temperatures indicate the potential for incomplete NO_x reduction in the catalyst and the formation of corrosive ammonium bisulfate. High gas temperatures indicate the potential for damage to the catalyst.

In SNCR systems, the gas temperature at the point of reagent injection should be monitored to be in the range of 1600°F to 1900°F (870°C to 1040°C). Low gas temperatures at the injection point indicate the potential for high ammonia slip emissions. At high gas temperatures, the conversion of NO_x ceases, and the reducing agent can be oxidized to form additional NO_x . Accordingly, at high gas temperatures, the emissions of NO_x can be higher than the concentrations that would exist without reagent injection.

Gas Static Pressure Drop - After correcting these data for changes in the gas flow rate, monitoring static pressure drop provides an indication of the physical condition of the catalyst bed. Static pressures above the normal range may indicate buildup of particulate matter within the catalyst bed.

Predictive Emission Monitoring Methods

PEMS are theory-based or empirical models that correlate the parameter inputs to emissions. Unlike parameter surrogates, PEMS estimate a quantitative measurement of the flue gas emissions. A number of inputs are necessary for PEMS determination. The advantages of parameter monitoring include low initial and operating costs, low maintenance and inspection, and reduced calibration procedures.

PEMS only provide an indirect estimate of the source emissions; therefore, additional testing may be required during periods of possible noncompliance and to correlate parameter surrogates to flue gas emissions. If data applied to PEMS is not taken over an extended time period, fluctuations and other variability may bias results. Processes and gas streams differ even between similar facilities; data applicable to one facility may not be applicable to another.

Potential Problems with Parameter Monitoring

Applicability is one type of problem that can exist with parameter monitoring systems. For example, a PEMS that is based on short-term data may not be applicable to the same process on a long-term basis. Changes in the configuration or operation of the plant can necessitate the revision to the PEM to ensure that it still correlates.

Another potential problem with parametric monitoring is the validity or strength of the correlation. If a model is developed for a facility, but does not take into account all possible operations at the facility, there can be problems with the correlation. For example, if the correlation failed to account for the opening and closing of an air damper, then the correlation may not be valid when the air damper is moved from the position that it was in when the correlation was developed.

Reliability of the parameter monitoring system — to ensure reliable and accurate data over time — is another potential problem. Reliability checks of extractive systems usually consists of periodic calibration gas checks. Techniques for evaluating reliability of parameter monitoring systems are discussed in the next section.

OXYGEN CONCENTRATION MONITORS

Monitoring Oxygen Concentrations

Most combustion systems limit oxygen concentrations in order to avoid localized high concentrations in the peak temperature zones where thermal NO_x can form. However, air infiltration into the combustion system can increase to substantial levels due, in part, to the frequent thermal expansion and contraction of the combustion system during start-up, shut down, and operating rate changes. The oxygen entering with the infiltrating air can increase the thermal NO_x formation rates. Improperly adjusted burners can have oxygen levels above the intended levels causing high NO_x formation rates because of the availability of the oxygen in the peak temperature zones.

Oxygen concentrations should be monitored so that the operator can determine if factors such as air infiltration or burner operational problems could be increasing NO_x formation rates. In reviewing these data, it is important to note that the normal oxygen concentrations are a function of the combustion system operating rate. Oxygen concentrations are at a minimum at full load and increase slightly as the load is decreased due to the need for higher excess air rates at low load. Accordingly, the present oxygen concentration data should be compared against baseline data for the combustion system-operating rate (load) at the time that the oxygen data is obtained.

In reviewing the oxygen concentration data, it is also important to note that the oxygen concentrations are often not spatially uniform at the measurement location. Problems caused by air infiltration or burner adjustment can create stratified gas streams with substantial differences in oxygen concentrations. Oxygen monitors sampling gas at only one or two locations in the duct or breeching might not accurately characterize the variations in the oxygen concentration across the gas stream. Accordingly, to the extent possible, the entire breeching or duct should be sampled with an oxygen monitor.

Measurement Techniques

Common oxygen analyzers for extractive systems include polarographic, electrocatalytic, magnetodynamic, magnetopneumatic, and thermomagnetic analyzers.

Electrocatalytic Technique Electrocatalytic analyzers are commonly called fuel cell analyzers despite the fact that fuel cells are no longer used for detection. Instead electrolytic concentration cells containing a special ceramic material are used for O_2 measurement. The ceramic material, consisting of zirconium oxide coated by a thin

layer of platinum, is heated to 850°C inside a small chamber. Reference gas having an ambient level O₂ concentration is introduced to one side of the ceramic material, while the sample gas passes through the opposite side of the chamber. Mass transfer creates a flow of the O₂ molecules across the ceramic media. As the O₂ molecules pass through the platinum they are catalyzed to O²⁻ ions. Because new sample is always being passed through the chamber, equilibrium is never established. An electrode on the sample side of the chamber measures the electromotive force created by the flow of electrons. Electromotive force can be related to the concentration of oxygen in the sample as shown in Equation 9-2.

$$\text{emf} = \frac{RT}{4F} \ln \frac{P_{\text{ref}}(\text{O}_2)}{P_{\text{sample}}(\text{O}_2)} \quad \text{Equation 9-2}$$

Where:

- emf = electromotive force
- R = Ideal Gas law Constant
- T = temperature of chamber
- P_{ref}(O₂) = partial pressure of O₂ in reference side of chamber
- P_{sample}(O₂) = partial pressure of O₂ in sample side of chamber
- F = Faraday's constant

Oxygen is one of the few gases that are *paramagnetic* (attracted to a magnetic field). Magnetodynamic, magnetopneumatic, and thermomagnetic analyzers are three common measurement devices that take advantage of the unique paramagnetic characteristic of O₂. NO and NO₂ are the only other paramagnetic gases encountered in CEM testing that, at very high concentrations, may create interference.

Magnetodynamic Technique The magnetodynamic technique measures the deflection of a dumbbell-shaped device set in a non-uniform magnetic field. The dumbbell-shaped device consists of two diamagnetic glass spheres connected by a rod. As sample gas containing oxygen passes over the glass dumbbell in the magnetic field, the spheres are deflected. The degree of deflection is measured and related to the concentration of oxygen passing through the detector.

Magnetopneumatic Technique In a magnetopneumatic analyzer, the sample gas is passed through an uneven magnetic field and the oxygen is drawn to the stronger side of the field. The resulting pressure differential is measured and related to the oxygen concentration.

Thermomagnetic Technique Thermomagnetic instruments relate the paramagnetic force of O₂ to a change in temperature. Sample passes by one end of a magnetized perpendicular tube. The oxygen is attracted to the magnetic field and passes through the perpendicular tube. As sample flows through the perpendicular tube, the temperature decreases. The amount of temperature change is monitored by a change in resistance and is related to the oxygen concentration.

EMISSIONS CALCULATIONS

Wet and Dry Basis

As illustrated in Problem 9-1, it is necessary to report concentration values as ppm_{vd} (dry-basis) or ppm_v (wet-basis). If the difference is not specified, substantial errors in emission calculations can occur. Equation 9-3 is used to convert from a wet basis to a dry basis, and visa versa.

$$C_{\text{dry}} = \frac{C_{\text{wet}}}{(1 - B_{\text{ws}})}$$

Equation 9-3

Where:

- C_{wet} = concentration on a wet basis (ppm_w)
- C_{dry} = concentration on a dry basis (ppm_d)
- B_{ws} = fraction of moisture in flue gas, %H₂O/100

All reported emissions involve two or more measurements. The measurements used to calculate emissions must be either all wet or all dry. For example, stack flow measurement is wet and it cannot be combined with concentration (ppm) data from a dry CEM system. You must either determine the dry stack flow or the wet concentration data to use them when reporting emissions such as lb/hr.

Dilution Correction

NO_x concentration readings will be reduced as a result of any in-leakage of air throughout the process or by increased excess air levels. NO_x concentration standards generally require concentration readings to be corrected using oxygen, carbon dioxide, or excess air in order to report emissions at a known (specified) dilution level. Examples of correction calculations are provided in Equations 9-4, 9-5, and 9-6.

$$C_{@7\%O_2} = C \left(\frac{20.9 - 7}{20.9 - \% O_2} \right)$$

Equation 9-4

$$C_{@12\%CO_2} = C \left(\frac{12.0}{\% C O_2} \right)$$

Equation 9-5

$$C_{@50\%EA} = C \left(\frac{100 + \%EA}{150} \right)$$

Equation 9-6

Where:

- $C_{@7\%O_2}$ = concentration corrected to 7% oxygen
- $C_{@12\%CO_2}$ = concentration corrected to 12% carbon dioxide
- $C_{@50\%EA}$ = concentration corrected to 50% excess air
- C = concentration of pollutant in flue gas
- $\%O_2$ = percentage of oxygen in flue gas
- $\%CO_2$ = percentage of carbon dioxide in flue gas
- $\%EA$ = percentage of excess air in flue gas

Some typical dilution levels, specified in the regulations for each type of source, are: 3% O₂ for boilers, 15% O₂ for combustion turbines, 7% O₂ for waste to energy combustors and incinerators.

Concentration Based Emission Rates

One of the most common and most useful emission reporting units is *pounds per million Btu* (lb/MMBtu). One reason for the prevalence of this dimension is that it is not necessary to measure the firing rate of the source to determine the emissions. All the necessary data can be acquired at the stack sampling location without relying on facility data. Lb/MMBtu and ppm corrected are closely related units and each can be calculated from the other if the dry F-factor (F_d) is known. So lb/MMBtu and corrected ppm are very nearly interchangeable ways of regulating and reporting emissions.

The formula for calculating lb/MMBtu from raw data is:

$$\frac{\text{lb E}}{\text{MMBTU}} = \frac{\text{ppmdv E}}{1,000,000} \times \frac{\text{Mw}_E}{385} \times F_d \times \frac{20.9}{20.9 - \%O_{2d}} \quad \text{Equation 9-7}$$

- where:
- E emission species (NO_x, SO₂, etc)
 - ppmdv measured parts per million dry volume
 - Mw_E molecular weight of species E
 - O_{2d} dry measured oxygen concentration in %
 - 46 the molecular weight of NO₂
 - 386 the number of cubic feet per pound mole
 - F_d the dry F-factor (see Table 9-2)

The same formula when the raw data is measured wet is:

$$\frac{\text{lb E}}{\text{MMBTU}} = \frac{\text{ppmwv E}}{1,000,000} \times \frac{Mw_E}{385} \times F_w \times \frac{20.9}{20.9 - \%O_{2w}}$$

Equation 9-8

Note that all the data and the F-factor must be either wet or dry - you must not mix wet and dry data.

Another way to compute lb/MMBtu emissions is to use a carbon balance (F_c) and measured CO_2 concentration. The formula is

$$\frac{\text{lb E}}{\text{MMBTU}} = \frac{\text{ppmv E}}{1,000,000} \times \frac{Mw_E}{385} \times F_c \times \frac{100}{\%CO_2}$$

Equation 9-9

In this case the measurements can be made either wet or dry, but both the pollutant E and the CO_2 must be measured the same way - don't mix wet and dry data.

The F-factor is the volume of combustion gas generated when one million Btu of fuel is burned with zero excess air. It can be determined from an ultimate analysis of the fuel – no other data is required. Default F-factors for a variety of fuels are provided in Table 9-2. The dry F-factor (F_d) is the dry gas volume, the wet F-factor (F_w) is the total combustion gas volume, and the carbon F-factor (F_c) is the volume of carbon dioxide. All volumes are in standard cubic feet.

Table 9-2
F-Factors for Various Fuels

Fuel	F_d (dscf/MMBtu)	F_w (wscf/MMBtu)	F_c (scf/MMBtu)
Anthracite Coal	10,100	10,540	1,970
Bituminous Coal	9,780	10,640	1,800
Crude Oil	9,190	10,320	1,420
Natural Gas	8,710	10,610	1,040
Propane	8,710	10,200	1,190
Wood	9,240	--	1,830

Source: 40 CFR 60 Appendix A, Method 19

Note that neither the stack gas flow rate nor source firing rate (MMBtu/hr) are needed to determine emissions in lb/MMBtu, despite the presence of MMBtu in the result. Note also the presence of dilution correction terms in all the equations – the pollutant concentration is corrected to 0% O_2 , the dilution level at which the F-factor is derived. These equations show that lb/MMBtu and ppm_{corr} are equivalent ways of expressing the emissions rate. Either one can be calculated from the other.

Emissions in lb/mmBtu can be determined using a basic CEM system that only needs to measure the pollutant (NO_x in this case) and either O₂ or CO₂.

Mass Emission Rates

Many sources, such as those covered by Part 75, must report emissions as a mass emission rate. Mass emission rates are expressed in terms of the mass of the pollutant per unit time, which in some cases is the relevant indicator of the amount of emissions released into the atmosphere. There are two approaches to determining mass emission rate: (1) stack flow x concentration, and (2) heat input x emission rate (lb/mmBtu). Method 1, we'll call in the stack flow method, can be used on any combustion source and does not rely on any data from the facility. All the data is reassured at the stack. Method 2, we'll call the heat input method, uses simpler measurements, but it relies on facility instrumentation for heat input. In practice this means that Method 2 may be preferred on sources fired with natural gas or oil, while sources fired with solid fuel or mixed fuels may be limited to using Method 1.

Method 1 – Stack Flow

Mass emission rate is the product of the stack mass flow rate and the mass concentration. Stack measurements of flow velocity, temperature and pressure must be converted to mass flow rate (lb/hr). Concentration measurements are volume based (ppm, %, etc.) and need to be converted to a mass basis (lb NO_x per lb flue gas) Furthermore, either the exhaust moisture content is needed to determine the dry stack flow rate using Eqn 9-3, OR, the NO_x concentration must be measured wet. Equation 9-7 incorporates the necessary constants to calculate the emissions rate from stack measurements. NO_x mass emission rates are based on the molecular weight of NO₂, because NO_x quickly converts to NO₂ in the atmosphere.

$$\text{Emission rate (lb NO}_x\text{/hr)} = Q_{\text{dscfh}} c_{\text{dry}} \left(\frac{\text{lb NO}_x}{8.375 \times 10^6 \text{ scf}} \right) \quad \text{Equation 9-10}$$

Where:

Q_{dscfh} = flow rate of flue gas at standard conditions (dscf/hr)

c_{dry} = dry measured concentration (ppm)

The dry standard flow rate of the flue gas can be calculated as shown in Equation 9-11.

$$Q_{\text{dscfh}} = A_s v_s \left(\frac{3600 \text{ sec}}{\text{hr}} \right) (1 - B_{\text{ws}}) \left(\frac{528}{T_s} \right) \left(\frac{P_s}{29.92} \right) \quad \text{Equation 9-11}$$

Where measured parameters are:

A_s = cross-sectional area of stack or duct (ft²)

v_s = flue gas velocity (ft/sec)

T_s = stack gas temperature ($^{\circ}R$)
 P_s = absolute stack gas pressure (in Hg)

There are two technical challenges with this approach. First, the average axial velocity in the stack is difficult to measure accurately. Second, since stack velocity is a wet measurement, the NO_x concentration must either be measured wet or, the gas moisture must be measured to allow calculation of the dry (moisture free) stack flow rate.

Method 2 – Heat Input

When the fuel has consistent properties and accurate measurements are available, then it's usually easier (and cheaper) to operate a CEM for NO_x and O₂ (or CO₂) than it is to measure stack flow in addition to the CEM for NO_x. Heat input is the product of the fuel flow rate times its heating value. So, for example, the heat input for a gas fired source would be:

$$\text{mmBtu/hr} = \text{gas flow (std ft}^3\text{/hr)} \times \text{HHV (mmBtu/std ft}^3\text{)} \quad \text{Equation 9-12}$$

Where gas flow would have to come from facility instruments/data system and heating value would be provided periodically by the gas supplier. Mass emissions rate is given by the equation:

$$\text{Emissions (lb/hr)} = \text{Heat Input (mmBtu/hr)} \times \text{Emissions (lb/mmBtu)} \quad \text{Eqn 9-13}$$

where the emissions in lb/mmBtu is determined from Eqn 9-7, 9-8 or 9-9.

Problem 9-1

A dilution system samples gas on a wet basis. The data acquisition system recorded an average calibration-adjusted reading of 1.25 ppm_v NO_x during the past 24-hour period. The dilution ratio is set at 150:1, and the moisture of the flue gas is 12% by volume. What is the flue gas concentration on a wet and dry basis for the previous 24-hour period?

Step 1. Determine the actual concentration of NO_x in the flue gas.

$$c = c_{\text{measured}} D_o = 1.25 \text{ ppm}_v \left(\frac{150}{1} \right) = 188 \text{ ppm}_v \text{ (actual)}$$

Step 2. Determine the actual dry concentration of NO_x in the flue gas.

$$c = \frac{c_{\text{wet}}}{1 - B_{\text{ws}}} = \frac{188 \text{ ppm}_v}{1 - 0.12} = 214 \text{ ppm}_{\text{vd}} \text{ (actual)}$$

Where:

D_o = dilution ratio

C_{WET} = concentration on a wet basis
 B_{WS} = moisture fraction

Review Exercises

1. A facility is required to install a CEM system. The sampling source location is downstream from a fabric filter and near a breaching duct. It has been determined that the flue gas is stratified. The system must be calibrated on a regular basis. What appears to be the most appropriate CEM system for this facility?
 - a. In-stack dilution sampled on a dry basis
 - b. In-stack dilution sampled on a wet basis
 - c. Out-of-stack dilution system
 - d. In-situ double-pass path system
 - e. In-situ single-pass path system
 - f. In-situ point system

2. What are common problems or disadvantages of point in-situ systems? (Select all that apply.)
 - a. Misalignment of optical components because of stack vibrations.
 - b. Increased routine inspection, maintenance and replacement of parts compared with extraction systems.
 - c. Calibration using gases is more difficult compared with path systems.
 - d. Inaccessibility to filter
 - e. None of the above

3. Match the CEM system with the appropriate specifications for testing and calibrations of that system.

a. Out-of-stack dilution system installed at a nitric acid facility (NSPS source)	i. 40 CFR Part 60 Appendix A
b. In-stack dilution system installed at a large electric utility facility	ii. 40 CFR Part 75
c. Source testing company RM CEM system	iii. 40 CFR Part 60 Appendix F
d. Extraction CEM system installed at an industrial steam generating source (NSPS source)	

4. An analyzer consists of an IR source that emits light through a rotating wheel. Half of the filter wheel allows gas of wavelength λ_1 to pass to the sample and half of the filter wheel does not allow gas of wavelength λ_1 to pass to the sample. The gas concentration is related to the alternating signals measured by a detector. Name this monitoring instrument.
- GFC
 - Differential optical absorption using optical filters
 - Differential optical absorption using moving slits
 - Polargraphic
 - Chemiluminescent
5. How are oxygen analyzers used for controlling and reporting NO_x emissions? (Select all that apply)
- Correct concentration values to a dry-basis
 - Correct mass emissions rate to 7% O_2
 - Monitor burner operation
 - Determining air infiltration
 - Limit thermal NO_x formation
 - Limit fuel NO_x formation
6. The following data was obtained from extraction CEM testing performed on a 60-inch by 48-inch duct.
- 1 % oxygen (dry)
 - 8% carbon dioxide (dry)
 - 9% moisture
 - 120 ppm NO_x (wet)
 - 20 ft/sec gas velocity
 - 242° F
 - 30.1 in. Hg stack pressure
- Determine the NO_x dry concentration corrected to 12% CO_2 .
 - Determine the NO_x emission rate in lb/hr.
-