**INSTITUTE OF
CLEAN
AIR
COMPANIES**

WHITEPAPER:
AMMONIA MEASUREMENT
FOR COMBUSTION SOURCES

PREPARED BY:

INSTITUTE OF CLEAN AIR COMPANIES EMISSIONS MEASUREMENT DIVISION

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ICAC

The Institute of Clean Air Companies, Inc. (ICAC) is the national trade association of companies that supply stationary source air pollution monitoring and control systems, equipment and services. It was formed in 1960 (under the name IGCI) as a non profit corporation to promote the industry and encourage improvement of engineering and technical standards.

The Institute's mission is to assure a strong and workable air quality policy that promotes public health environmental quality, and industrial progress. As the primary representative of the air pollution control and monitoring industry, the Institute seeks to evaluate an despond to regulatory initiatives and establish technical guidance for the benefit of all.

1.0 INTRODUCTION

This publication provides as overview of the existing ammonia measurement technologies available to evaluate ammonia slip from combustion sources.

Nitrogen oxide (NO_x) emissions contribute significantly to the national environmental problems, including acid rain, photochemical smog (ozone), and elevated fine particle levels. Ozone exposure is linked to a number of adverse health effects, including significant decrease in lung function, airway inflammation and increased respiratory symptoms.

The U.S. Environmental Protection Agency (EPA) under the authority of the Clean Air Act (CAA) regulates NO_x emissions, a contributor to ozone formation. The regulations were developed in response to ozone issues that spurred the applications of several post combustion NO_x reduction technologies, including Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). Both technologies require the injection of ammonia and or urea to drive the chemical reaction necessary to reduce NO_x from the flue gas of a combustion source. In the SCR process, the reaction chamber contains a catalyst bed where NO_x from the flue gas is reduced to nitrogen (N_2) and water (H_2O) by the reaction of NO_x and ammonia (NH_5). Depending on the amount of dust, type, and concentration of acidic gas components in the flue gas, the SCR process normally operates in the temperature range of 250°-400°C. The primary reactions occurring in an SCR are given below:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

$$2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$$
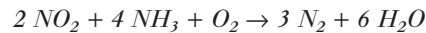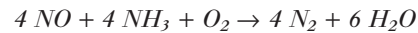
In the SNCR process, a reagent, typically urea or anhydrous gaseous ammonia, is injected into the hot flue gas, and reacts with the NO_x, converting it to nitrogen gas and water vapor. Unlike the SCR no catalyst is required for this process. Instead, it is driven by the high temperatures normally found in combustion sources at temperatures of about 800°C to as high as about 1200°C.

Ammonia slip is the excess un-reacted reagent that exists from the SCR or SNCR systems. It is undesirable because it is a pollutant and because it can have harmful effects on downstream plant equipment. Because any ammonia that does not contribute to NO_x reduction in an SCR will generally become ammonia slip, the efficiency of an SCR system can be determined by monitoring the outlet of excess ammonia. This is not so with SNCR because the urea or ammonia can undergo competing chemical reactions at the higher temperatures. It is important to maintain the level of ammonia slip to low levels, so as not to cause operational problems or pollutant emissions from the combustion source.

Ammonia slip is measured after the NO_x reduction equipment. In circumstances where combustion sources experience a high level of ammonia slip, the excess un-reacted ammonia can contribute to increased corrosion, fly ash contamination, increased formation of ammonium salts on the air pre-heater and other downstream surfaces and emission of gaseous ammonia.

Steps that are taken to minimize ammonia slip from NO_x control systems include: process design, process optimization, and maintenance of strict operating procedures. As an example of process design, the sizing of an SCR catalyst is determined by the need to reduce NO_x while also maintaining adequately low ammonia slip. Once installed, these SCR systems undergo an initial optimization to ensure that the SCR system operates. Ammonia slip is an important performance parameter that is measured during these optimization tests. Once in operation, the SCR is only operated within the operating conditions it was designed for in order to maintain both NO_x emissions and ammonia slip to adequately low levels. SCR systems achieving 90 percent or greater NO_x reductions operate with ammonia slip values below 5 parts per million (ppm). Ammonia slip has been controlled to below 2 ppm through proper design and use of sufficient catalyst.

In the case of SNCR process optimization there is a trade off between reagent utilization and ammonia slip as a function of temperature in the furnace. Ammonia slip is controlled by careful injection of the reagent into specific regions of the furnace or other sources where proper conditions (temperature, residence time, and NO_x concentration) for the SNCR reaction can be maintained.[1] In the absence of the proper conditions, un-reacted ammonia can be emitted. Ammonia slip will likely result if the reagent injected over treats some areas of the furnace or if the reagent is injected into a cool region of the furnace where the chemical reactions are very retarded.

1.1 Benefits of Monitoring Ammonia Slip

Monitoring ammonia slip provides both operational as well as economical benefits. Ammonia slip is undesirable as a pollutant as it can contribute to fine particulate matter (PM), equipment corrosion problems, strong

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[1]ICAC White Paper on Selective Non Catalytic Reduction (SNCR), February 2008

ammonia odor, nitrification of aquatic systems as well as contributing to the contamination of fly ash. Although ammonia slip is normally well controlled, operating transients, power outages and equipment failures can cause ammonia slip to increase to well above expected levels. Continuous measurement of ammonia slip can identified non-ideal conditions allowing for operational corrective action measures to be taken early enough to avoid the undesirable effects of high ammonia slip.

When under an allowance trading regulatory regime any additional NO_x reduction below a preset level has an economic value that can be traded for monetary benefit. Lower NO_x levels can be obtained by monitoring ammonia slip. NO_x control systems are normally designed with some safety factor in order to avoid high ammonia slip while maintaining adequately low NO_x emissions. For instance, a new SCR catalyst is generally capable of much higher NO_x reductions (while maintaining low ammonia slip) at the beginning of its deployment than at the end of the design period. With an ammonia slip monitor it is possible to control the operation parameters to achieve greater than designed NO_x reduction when the catalyst is relatively new providing economic recovery value in a NO_x trading schema for a portion of the catalyst lifetime.

1.2 Drivers for Installing Monitoring Technology

Environmental requirements have been the primary driver for the installation of monitoring technology. Under the 1970 Clean Air Act (CAA), fossil-fuel fired steam generators were the first source category required to be monitored to ensure emission control systems met specified performance levels. Since 1970, the 1990 Clean Air Act Amendments established requirements under Titles I and Title IV that initiated additional NO_x controls to include SCR and SNCR. As a result, nearly half of all coal-fired generating capacity and virtually all combined cycle gas turbine capacity is equipped with post-combustion NO_x controls that could produce ammonia slip.

2.0 COMBUSTION PROCESS CONDITIONS

When selecting the proper ammonia measurement approach, it is necessary to consider the purpose of the measurement and the particular process conditions at the point of measurement. If the measurement is for compliance purposes, that is stack emissions requirements, the measurement must be made at the chimney or at another location that the permitting authority determines will provide an indication of stack emissions. For process optimization, it may be better to measure ammonia slip farther upstream in the process as the ammonia may react or change its form between the NO_x reduction process outlet and the emissions stack outlet.

2.1 Temperature

For process control, ammonia slip should be mea-sured after the NO_x reduction process, with the precise location determined by the application. However, for clean fuel applications, such as natural gas, the slip can be measured at the stack as this will normally be indicative of the ammonia slip leaving the NO_x control process.

For coal and other fuels which have particulates or sulfur in the exhaust, ammonia slip from these application processes are ideally measured at temperatures above the ammonium sulfate or ammonium bisulfate formation temperature. For a boiler this means measuring ammonia upstream of the economizer in the temperature range of about 300°-350°C. In most cases this location is upstream of particulate removal making it a difficult measurement which must be done in a hot, dusty environment where there are many contributors that may cause interferences.

2.2 Interference Sensitivity

When selecting an ammonia measurement method, it is necessary to consider the possible interferences to the measurement. An interference is something that will affect the accurate measurement of the required analyte. For example, UV-based ammonia measurement methods are often sensitive to SO_2. One might not want to use a UV based method to measure ammonia in the presence of high amounts of SO_2 without having made some provision for addressing the possible interference. Infrared based ammonia measurement methods (which include tunable diode lasers, non-dispersive and dispersive infrared system) are sensitive to water vapor, so it needs to be considered when evaluating this approach. NO_x analyzer based methods for the detection of ammonia (usually using chemiluminescence analyzers) are obviously sensitive to NO_x therefore the levels of NO_x relative to the expected ammonia slip need to be factored in when considering this approach.

This Whitepaper presents each of the ammonia analyzer methods describing the advantages as well as disadvantages for the analysis of ammonia.

3.0 AMMONIA MEASUREMENT TECHNOLOGY DESCRIPTIONS

3.1 Tunable Diode Laser (Infra Red) Measurement Technology

Tunable Diode Lasers (TDL's) have special properties based upon small crystals (about 0.1 mm^2) made of a mixture of elements such as gallium, arsenic, antimony and phosphorus. The proper selection and proportion of these elements the crystal can be made to emit at wavelengths where the target gas, (NH_3 in this application) absorbs radiation of a particular energy. Changing either the temperature or current through the laser permits the wavelength to be tuned over the selected absorption feature of the target molecule. When an electric current is passed through these crystals they emit very pure laser light in the near infrared spectral region.

The temperature of the laser is stabilized with a thermal electric cooler and the wavelength can be changed to sweep across absorption band by changing the current pass through the laser at a rate of several hundred hertz. The laser current is simultaneously modulated in the megahertz region so that phase sensitive detection techniques may be used to improve sensitivity.

One advantage of the TDL technology is that the presence of the measured component in the gas stream can be used as a reference point for the laser itself. This function is called "line locking" and consists of the absorption peak of the NH_3 being used to keep the laser at the desired frequency. However, in the absence of the measurement component, during bypass or scheduled shutdowns, the laser can drift, and be outside calibration when the measurement component returns. To avoid this drift, many TDLs can be supplied with a sealed internal reference cell, which contains a known amount of the gas to be measured. The use of the reference cells allows for both line locking of the analyzer, but also the ability to continuously monitor the instruments calibration.

System Configuration typically consists of the Analyzer unit in either stand alone or 19″ rack mount configuration, which contains the TDL and associated electronics for signal transmittal and signal analysis. The Optical heads which contain the Launch and Receive components are mounted on the duct or stack and connected to the Analyzer via Fiber Optic/Coax cabling. This permits the analyzer to be placed in any suitable location, such as the CEM shelter or control room of the plant where it is not subjected to harsh climatic environments and where it can be readily serviced as required. The optical signal can be transported from the instrument to the measurement location by fiber optics and the return detected signal transported to the instrument by a separate coaxial cable. Thus, for example, continuous measurements can be made of the emissions in stacks and ducts which can be as much as 1500 feet (with PDA) away from the instrument.
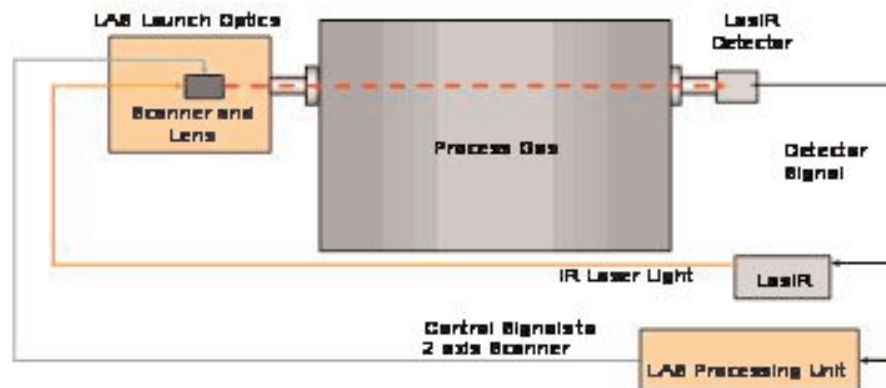
Figure 1.   Cross Duct System Design

Multi-point array monitoring systems are also available with these systems allowing for a number of locations to be monitored from a single analyzer. The laser light signal is either multiplexed to prevent the loss of light intensity or passed through a beam splitter which will reduce the power of the laser; each method will determine the number of locations that can be monitored by a single analyzer for various applications. This allows for an array of detectors to be mounted on the stack or duct for measurement in a turbulent area or for SCR grid ammonia injection tuning. Moreover, the use of optical multiplexing techniques offers a cost effective method for multiple point monitoring.

In addition to the cross-duct systems designs illustrated above, there are TDL analyzers available in a probe configuration. While limiting the area measured, these probes offer some advantages in applications where high dust concentrations can pose attenuation issues for the TDL, like after an SCR. The probe versions can also be applied to applications where alignment is a problem for cross duct versions. The probe can be supplied with

an open measurement path, or with a filtered measurement path. The filter is typically ceramic with a filter value of 1 micron size. Care should be taken when specifying a filtered probe in applications where the process temperature can drop below 490°F, as there could be lose of NH_3 on the filter itself. This is generally not an issue in applications such as SCR outlet, where the temperatures are above 500-600°F.

3.1.2 Measurement Location

For process control the measurement is normally made at the outlet of the SCR or, for an SNCR, downstream of the economizer and upsteam of the air preheater. If the measurement is being made for stack emissions monitoring, it is on the stack or at another location that would be considered representative of stack emissions.

The measurement sensitivity is dependant upon the measuring path length and the opaqueness (particulate matter density) of the gas stream. The path length distance between the light source and the detector can vary depending upon the sample steam's particulate concentration. Therefore, when choosing the measurement location these factors along with the turbulence and stratification issues that arise must be considered. The measurements are usually made in-situ across the stack or duct. Various configurations can be chosen to define the process interface by the choice of flange sizes, materials, purging modes and purging media, in order to adapt the sensors for process engineering measurements. In some cases the optical path can be inside a probe; however, this will limit the path length.

Alignment of the optical heads are of significant importance and therefore the sight tubes to which the optics are attached are required to be aligned to specific tolerance typically within 1 degree and must be maintained at relative high temperatures. The optical heads must have the capability to adjust for any small misalignment errors.

Another component that must be taken into account is the "thermal growth" of the duct or stack and material aging. Several engineered solutions are available to counteract this issue.

Two methods are employed for measurements across stacks or ducts; 1) single-pass where the laser radiation is transmitted across the stack to the detector on the other side, and 2) dual-pass where the laser radiation is transmitted across the stack to a reflector and then back to the detector on the same side as the transmitter. In typical installations instrument air is used at each of the optical lenses to keep them clear of flue gas contaminants. In special situations where long spool pieces or lagging is employed especially in the prescience of negative pressure stacks or ducts, blowers are required to prevent the migration of ammonia in the spool pieces. Such migration would cause a variable and inconsistent concentration of ammonia in the laser path resulting in inconsistent and inaccurate measurements. Thus, applying a positive pressure of ambient air to the spool pieces will assure that no stack gas ammonia is migrating into the spool pieces.

Particular attention must also be paid to the location of the measurement tools to limit the accumulation of particulate matter which can not only cause loss of signal due to light scattering but also can result in physical changes in the alignment of the laser light requiring realignment after cleaning.

3.1.3 Sensitivity and Detection Limit

The sensitivity and minimum detection limit of an absorption device are path length dependent. The longer the path length, the higher the absorption and the lower the sensitivity and detection limit. Therefore, longer path lengths result in better detect ability of low concentrations.

Dust loading in the effluent stream has the effect of blocking and scattering the laser radiation such that the detection limit will be compromised, leading to a much higher minimum detection value, due to lower power levels of the laser radiation reaching the detector. While particulate matter affects the detection limit, most systems can tolerate laser radiation power reductions of up to 90% without affecting the accuracy of the measurement. Nevertheless, there is a trade off in path length considerations between detect ability and reliability of the measurement. A single pass system with PDA is recommended for high dust applications.

Water vapor is also active in the near IR spectral region, and some diode laser based analyzers have a significant sensitivity to water vapor as well as ammonia. The ammonia absorption line used by the particular instrument determines the degree of interference from water vapor. The interference from the water vapor signal is reduced by the development of algorithms used to address this interference.

Typical detection limits on coal fired boilers dependant on the above criteria would be +/- 1ppmv with a detection limit of 0.3 part per million by volume (ppmv).

3.1.4 Calibration Requirements

Prior to initial usage the instrument must be calibrated for ammonia using the standard EPA single component calibration technique. The standards will need to be created using a National Institute of Standards and Technology (NIST) certified permeation tube system that requires tightly controlled heater ovens and at least two mass flow controllers (MFCs) to blend the starting concentration down from 100 ppm to 1 ppm. The assumption is that below 1 (ppm) the TDLA response will be linear.

After the initial calibration is performed system validation is performed on a regular basis as defined by the governing body. The calibration cell can be a sealed cell with a known concentration of ammonia traceable to NIST, which is used for line checks or to comply with any regulatory need for daily checks.

3.1.5 Maintenance Requirements

Daily checking for alarms or status signals of the following items will indicate proper running of the instrument:

- Laser Power
- Signal strength
- Peak Signal
- Laser Temperature

To ensure that the air purging system is still in good operating condition monthly checks should be performed on the filters, pressure supply, optical purge line as well as making sure the optics in the stack are being kept clean. Finally, a verification of the optical alignment in the stack should be done on a quarterly basis.

3.2 Measurement of Ammonia Slip Using NO_x Differential Method

3.2.1 Inlet/Outlet Differential NO_x Method

The calculation of ammonia slip using the inlet/outlet differential NO_x method along with ammonia flow rate and stack flow calculation is common in the industry. This method has been employed successfully in many EPA permitted CEMS, for control and compliance monitoring. This method is reliable and low in cost for sources where SCR inlet monitoring is preferred or a requirement. Unlike the stack ammonia monitoring methods, it allows the user to have a measured inlet NO_x reading for SCR control and meet the regulatory requirement for reporting NH_3 slip.

The inlet/outlet method is used where SCR control is also a requirement since both the SCR inlet NO_x and SCR outlet NO_x are measured on a continuous basis. The outlet measurement is the usual CEMS compliant system. The inlet system requires a second probe mounted on the duct before the SCR and a second NO_x analyzer.

The NO_x and NH_3 react on a 1:1 basis, therefore, the amount of NH_3 reacted is equal to the amount of NO_x reduced in the SCR. The simplified formula is:

$$NH_3 \text{ slip} = NH_3 \text{ fed} - (NO_x \text{ in} - NO_x \text{ out})$$

This calculation is performed by converting the NH_3 flow to the SCR usually given in pounds per hour to a volumetric part per million (ppmv) value using the heat input calculated from fuel flow and oxygen content. This simplifies the calculation since the two NO_x values are measured directly in ppm. Others sometimes solve for NH_3 slip using mass flow molar values which requires the calculation or measurement of stack flow.

The formulas using the volumetric method then become:

$$NH_3 \text{ lb/hr} = NH_3 \text{ lbs/mmBTU} * \text{Heat Input mmBTU/HR}$$

$$\text{Heat Input} = (\text{Fuel Flow} * HHV) / 1000000$$

$$NH_3 \text{ lbs/mmBTU} = NH_3 \text{ inlet ppm} * \text{Fd Factor} * 4.4096\text{x}10\text{-}8 * [20.9/(20.9 - O2 \%)]$$

The 4.409 (K-factor constant) corrects for the molecular weight of ammonia.

$$NH_3 \text{ lb/hr} = NH_3 \text{ Injection rate} * (NH_3 \text{ conc. } \%/100)$$

Solving for NH_3 inlet ppm, the equation becomes:

$$NH_3 \text{ inlet ppm} = ([NH_3 \text{ injection rate, lb/hr} * (NH_3 \text{ concentration, } \% \text{ by wgt}/100)] /$$
$$[\text{Heat Input, mmBTU/hr} * \text{Fd factor} * 4.4096\text{x}10\text{-}8]) * [(20.9 - O2 \%)/20.9]$$

3.2.2 Measurement Method

Depending on the type of combustion source and the kind of fuel being burnt will determine the method of measurement for NO_x that can be used for maximum benefit with respect to accuracy, maintenance, while taking into account the source permit requirements and local regulatory considerations.

Several types of configuration for the Monitoring System can be used, in all instances the system will require the sample to be conditioned so that any contaminants or interfering gases can be removed from the sam-

ple and presented to the analyzer so as to allow an accurate measurement.
Most common systems used are:

Fully Extractive:
Unconditioned sample transported to a remote location for conditioning and analysis, this method is typical for Gas Fired applications where low concentrations of NO_x are the norm and particulate matter and other contaminants' are low.

Dilution Extractive:
Sample is conditioned at the sample location by diluting the sample with an ultra clean air supply, typically by 100-200:1 then transported to a remote location for analysis. This method is used for heavy particulate laden gas streams such as from Coal fired or Biomass fueled Boilers. It can also be used in Incineration applications when dangerous contaminants are present.

In-Situ:
The measurement is made at the sample location, depending on the fuel type and boiler layout, this will allow for a faster response if feed back to the SCR controls are being considered.

In most instances a Chemiluminescence Analyzer is used as the measurement type due to the accuracy and reliability of this method of measurement, but other methods such as UV, FTIR, ZrO_2 and NDIR can be used. In all cases a NH_3 scrubber is used for the SCR outlet measurement to ensure no fouling of the sample system.

Chemiluminescence (Chemical Light) a measurement technique for NO/NO_x that measures the light given off as a result of the reaction between NO and Ozone. The light output is proportional to the concentration of NO. NO_2 is converted to NO using a high temperature catalytic converter. NO_2 does not react with Ozone so it must be converted to NO.

3.2.3   Measurement Location

Typically, NH_3 is measured in two places in a combustion process:
1) On the outlet of a NO_x control system, such as an Selective Catalytic Reduction (SCR) or Selective Non-Catalytic Reduction (SNCR). The measurement of NH_3 in this location is to determine the amount of "slip" that is escaping from the reaction process. The SCR is usually located near the end of the process, prior to an flue gas desulfurization (FGD) or the stack. The SNCR process is typically done by injecting NH_3 directly into the boiler. Excess NH_3 slip can be a problem for several reasons. One, a company may wish to optimize their SCR/SNR process. Slip increases costs due to overuse of NH_3, and fouling of saleable fly ash. Secondly, high levels of NH_3 can lead to corrosion and maintenance issues with process after the injection, such as air exchangers, etc.
2) On the stack as part of a CEM system. In general, NH_3 is not a commonly regulated gas; however it is becoming a more prevalent requirement in certain states, such as Texas, and certain industries, such as glass plants.

Due to the multi-component nature of both the IR and FTIR analyzers, their benefits typically lie in the CEM application, where NH_3 can be easily added to a system already monitoring other regulated gases such as SO_2, NO_x, CO, etc.

3.2.4   Sensitivity and Detection Limit

Most Chemiluminescence Analyzers have the capability of dual ranges, in these analyzers the typical minimum detection limit is in the 40-60 part per billion (ppb) range with a drift of $< 1\%$ of reading.

3.2.5   Calibration Requirements

As with CEMS systems, these analyzer systems are designed to be automatically calibrated with span gas on a daily basis.

3.2.6   Maintenance Requirements

With any Extractive sampling system, there will be a general maintenance routine, that is required and when alarms or analyzer drift is noticed.

3.3 Chemiliminescence NO_x Differential Method

Differential NO_x/NH_3 Converter method of ammonia measurement by chemiluminescence actually determines the ammonia concentration of the gas by comparison of the nitric oxide (NO) concentrations in two gas sample streams. One of the gas sample streams undergoes a conversion which changes the ammonia to nitric oxide by an amount proportional to the ammonia concentration plus the nitric oxide concentration originally in the gas.

The other gas stream remains unaltered. The amount of nitric oxide in each stream is measured by the principal of chemiluminescence. Comparison of the two nitric oxide concentrations is then an indication of the amount of ammonia in the original gas stream. The system consists of a single probe with two sample paths, an ammonia converter and two nitric oxide analyzers. In the ammonia converter, the gas stream passes through an oxidation catalyst operating at high temperature. The NH_3 in the stream is oxidized by the catalyst to an amount of NO proportional to the amount of NH_3 in the sample. The equation of this oxidation reaction is:

$$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$$
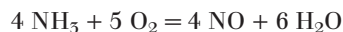
Both the converted and unconverted gas streams are then passed through to their respective chemiluminescence analyzers which determine the amount of NO present in each sample stream, the NO_x analyzers are identical in range, manufacturer, and model number. The unconverted gas sample contains only the original concentration of NO. The difference in NO content between the two sample streams represents the content of NH_3 in the stack gas as given by the equation:

$$NH_3\ slip\ (ppm) = NO_x\ (ppm)\ (total\ converted) - NO_x\ (ppm)\ (unconverted)$$

Since NH_3 is extremely water soluble and tends to "stick" to the tubing and sample probe materials commonly found in extractive CEMS, the two sample streams are treated differently to avoid any NH_3 from sticking to the probe as well as the sample line, in the stream that is used to analyze for NH_3. Heated electropolished stainless steel line should be used to reduce the chance of NH_3 sticking to the surface. This stream is then passed over an electrically heated oxidation catalytic converter which converts NH_3 into NO_x, while the NO_x stream uses an ammonia scrubber to remove the NH_3 prior to the stream reaching the detector.

In theory, the catalytic conversion process should have a 100% conversion efficiency (i.e. all NH_3 molecules are converted to NO). In actual practice however the NH_3 conversion process has an efficiency of only 90-98% depending on the sample flow rates, type of converter, and NH_3 concentrations. Conversion efficiencies of 95%+ can be expected on typical combustion turbine applications.

3.3.1 Measurement Method

Several configurations for the Monitoring System can be used. In all instances the system will require the sample to be conditioned so that any contaminants or interfering gases can be removed from the sample and presented to the analyzer to allow accurate measurements. The most common measurement method is the extractive method.

In general, NH_3 is a very water soluble compound, and readily forms salts at lower temperatures. As is the case of any extractive method system (TDLAs, FTIR, NDIR and UV-VIS included) the potential formation of salts makes the task of sample handling more challenging and critical to the success of the NH_3 measurement system. Every effort should be made to keep the sample line and probe as hot as possible from the point at which the gas is sampled all the way to the exist of the gas sample cell. Sample probes should be equipped with heated heads and the sample line should be capable of maintaining temperatures near to or above 180°C. Careful installation of the sample line to ensure no sags is crucial (See ICAC's **EM-4 Guidelines and Recommended Practices for Preparing Bid Specifications and Bid Evaluation for Sample Transport Bundle**). Once the gas enters the analyzer cabinet, a heated pump and heated filters are used to avoid "cold spots". By keeping the sample gas heated above 180°C keeps the NH_3 in the gas phase and the formation of ammonium bisulfate and other salts can be suppressed. The use of a heat pump may not be necessary if the sample is pulled through the system.

Unconditioned sample transported to a remote location for conditioning and analysis, this method is typical for Gas Fired applications where low concentrations of NO_x are the norm and particulate matter and other contaminants' are low.

In most instances a Chemiluminescence Analyzer is used as the measurement type due to the accuracy and reliability of this method of measurement, but other methods such as UV, FTIR, NDIR and ZrO_2 can be used.

Chemiluminescence (Chemical Light) a measurement technique for NO/NO_x that measures the light given off as a result of the reaction between NO and ozone. The light output is proportional to the concentration of NO. NO_2 is converted to NO using a high temperature catalytic converter There are also low temperature Molybdenum (Mo) converters that are also used. NO_2 does not react with ozone so it must be converted to NO.

3.3.2 Measurement Location

Typically, NH_3 is measured in two places in a combustion process. For process control the mea-surement is normally made at the outlet of a NO_x control system, such as an SCR or SNCR or on the stack as part of a continuous emission monitor (CEM) system.

The measurement of NH_3 is performed at the process control location is to determine the amount of "slip" that is escaping from the reaction process. The SCR is usually located near the end of the process, prior to a FGD or the stack. For the SNCR process NH_3 is typically injected directly into the boiler. Excess NH_3 slip can be a problem for several reasons. The main reason is to optimize the SCR/SNCR process to reduce cost which can increase due to overuse of NH_3 as well as the fouling of fly ash that may be sold off after removal. High levels of NH_3 can also lead to corrosion and maintenance issues further in the process, such as air exchangers, etc.

At the stack NH_3 measurement are made to ensure that the effluent being released conforms to the maximum allowable release levels as defined by the EPA as part of a CEM system. In general, NH_3 is not a commonly regulated gas in the United States, however that is beginning to change as more states as well as and certain industries begin to require NH_3 monitoring. Since this technique also measures NO_x the stack location is a good choice for this analyzer.

3.3.3 Sensitivity and Detection Limit

Most Chemiluminescence Analyzers have the capability of dual ranges, in these analyzers the typical minimum detection limit is in the 40-60 ppb range with a drift of $< 1\%$ of reading.

3.3.4 Calibration Requirements

Prior to initial usage the instrument must be calibrated for ammonia using the standard EPA single component calibration technique. The standards will need to be created using a NIST certified permeation tube system that requires tightly controlled heater ovens and at least two mass flow controllers (MFCs) to blend the starting concentration down from 100 ppm to 1 ppm. The assumption is that below 1 ppm the system response will be linear.

As with other CEMS systems these analyzer systems are require calibration check with a certified calibration gas. It is suggested to challenge the system periodically with an NH_3 calibration standard using a cylinder with NH_3, balance air, which is representative of the desired range of measurement of NH_3 slip. This can be done during the standard Relative Accuracy Test (RATA) for the CEMS if applicable.

3.3.5 Maintenance Requirements

As with any Extractive sampling system there will be a general maintenance routine, typically unless any alarms or analyzer drift are triggered, this will consist of quarterly system checks including filters, pumps etc.

3.3.6 Performance Monitoring Method

Based on the need to maintain the highest accuracy of the measurement since the concentration levels are typically low ppm, then as with CEMS these systems can be subject to the typical quarterly audit standards used for compliance monitoring systems.

3.4 Multicomponent–NonDispersive IR and FTIR

The use of Non-Dispersive - Infrared (NDIR) and Fourier Transform Infrared (FTIR) analyzers for monitoring NH_3 is a well established continuous emission monitoring technique. Unlike Chemiluminescence, the NDIR and FTIR can determine the Ammonia (NH_3) concentration directly from the gas phase without pretreatment (ie, removal of moisture) or conversion of the NH_3. A big advantage of both techniques, is that they are able to measure multiple components, up to 12 for the NDIR and up to 30 for the FTIR in addition to NH_3, limiting the cost of system monitoring analytical equipment procurement.

Both NDIR and FTIR systems use infrared (IR) light which is directed into the gas sample and then absorbed. All molecules that have a dipole moment are considered to be "active" in the infrared region. A dipole moment is created when you have at least two atoms that are dissimilar whereby one of the atoms pulls the electrons that surround the other atom closer to it creating an imbalance, therefore single atoms such as helium (He) and argon (Ar) as well as diatomics like nitrogen (N_2) and hydrogen (H_2) are not visible in the IR region. When the irfrared light is then directed to an IR active gas molecule it will begin to vibrate as well as rotate at specific frequencies that are directly related to the chemical make up of that particular molecule. Molecules have specific areas in which there responses will show up, methods can be developed to use those peaks to clearly define the presence of those components. The IR response based up on the absorbance of the IR light that was put into the gas phase is directly proportional to the concentration of that particular molecule in the gas phase. The stronger the dipole moment is, the strong the absorbance of the IR light. It is from this response that the NDIR and FTIR are able to directly determine the concentration of the NH_3 gas within the stack gas.

System configuration typically consists of the Analyzer unit in either stand alone or 19″ rack mount configuration, which contains the NDIR or FTIR and associated electronics for signal transmittal and signal analysis. The gas sample is extracted from the emissions stack using a gas sampling system which typically consists of a heated sample probe, heated particle filter, heated sample line leading to a heated sampling pump which is positioned either in the front of gas sample cell, pushing the gas into the cell or at the outlet the gas sample cell where the sample is pulled through the gas cell. This permits the analyzer to be placed in any suitable location, such as the CEM shelter or control room of the plant where it is not subjected to harsh climatic environments and where it can be readily serviced as required. The optical signal is created at the system itself so the key to the success of this type of analysis is the extractive sampling system. Once acquired the signal can be easily transported from the system to a data control center for continuous monitoring as well as for control status. Response times are in seconds and in some systems the response can be in the millisecond range.

3.4.2   Non-Dispersive Infrared (NDIR)

Non-dispersive or filter-based IR systems utilize either the "Dual Wavelength / Filter" or "Gas Filter Correlation (GFC)", Cross Flow Modulation techniques to measure gas components. For NH_5, GFC is the technique of choice for some CEMS suppliers. In this case, both sample and reference filters are swung into the light path. In the case of the reference filter, typically nitrogen, or some other gas with no absorbance in the IR region, is passed through the gas cell, leaving a baseline background for comparison. Then the sample gas is run through the gas cell and the sample filter is swung into the light path allowing only a narrow band of light at a specific wavelength region to pass through to the detector, measuring the absorption of the gas that is specific for that filter in question.
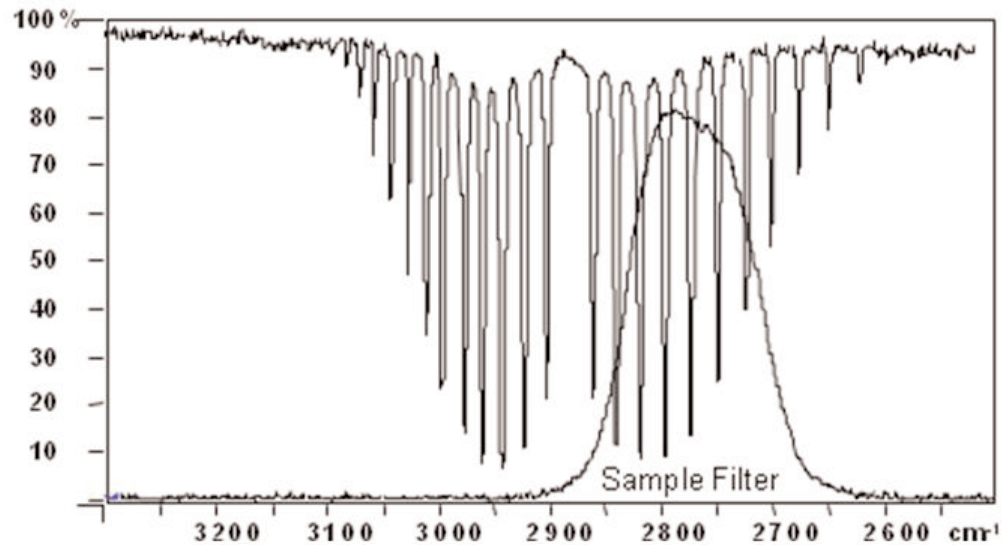

Figure 2.   Absorption Spectrum Illustrating Gas Filter Correlation Technique

The background interference is eliminated by rationing the sample absorbance to that of the reference (N_2) absorbance, as they are present in both spectrum. The cross interference from other gas molecules that will be present in the analysis gas, such as moisture in effluent gas, stream are reduced or eliminated by the region selection of the filter. The NDIR can monitor additional gases such as NO, NO_2, CO_2, CO, SO_2 and others by the application of multiple filters tuned to those compounds, providing a more versatile analysis instrument. Over time the GFC wheels can become fogged, leak gas and contribute to optical misalignment due to vibrations. Figure 3 offers a typical GFC configuration for review.
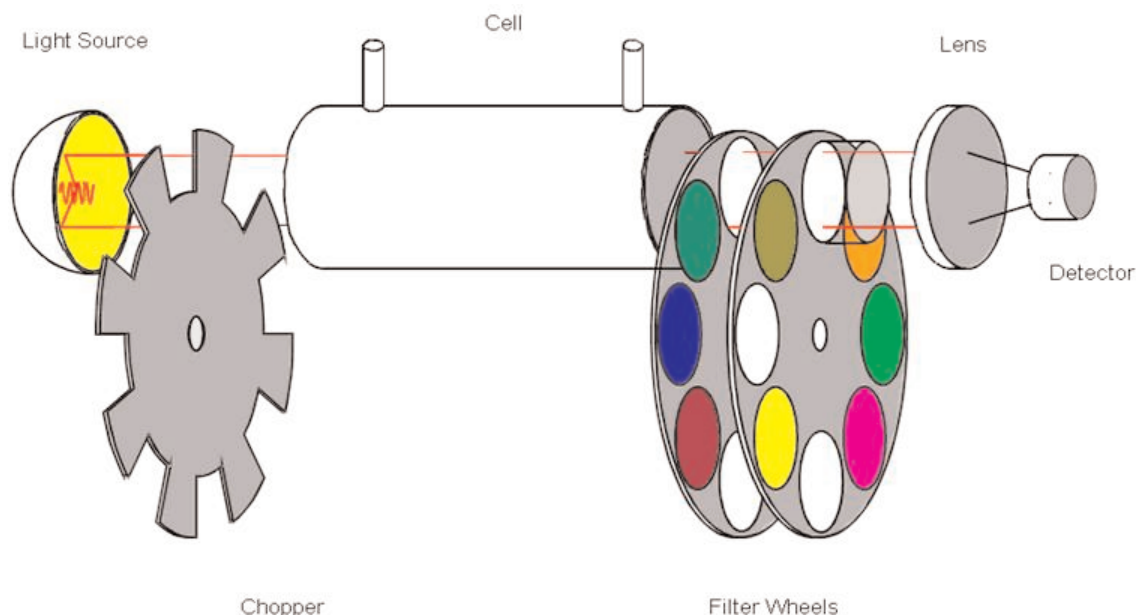
Figure 3.   NDIR Measuring Principle

3.4.3   *Fourier Transform Infrared (FTIR)*

Fourier Transform Infrared (FTIR) spectroscopy is a measurement technique for collecting all of the infrared spectral information at once. Instead of selecting a specific wavelength or region within the infrared region like NDIR, which is then used to record the amount of energy absorbed when the frequency of the infrared light is varied (monochromator), the FTIR light source uses all the frequencies in the IR region at once. The broadband IR light is then guided through the main heart of the FTIR instrument, the interferometer. The interferometer takes the broadband IR light and modulates all of the light wavelengths at the same time. Once modulated, this signal is passed through the gas cell where the various molecules absorb some of the light, resulting in a measured signal (or interferogram) where they can be deconvolved using the Fourier Transform process which converts the mirror position into a frequency response that is related directly to the molecules present in the gas sample cell.
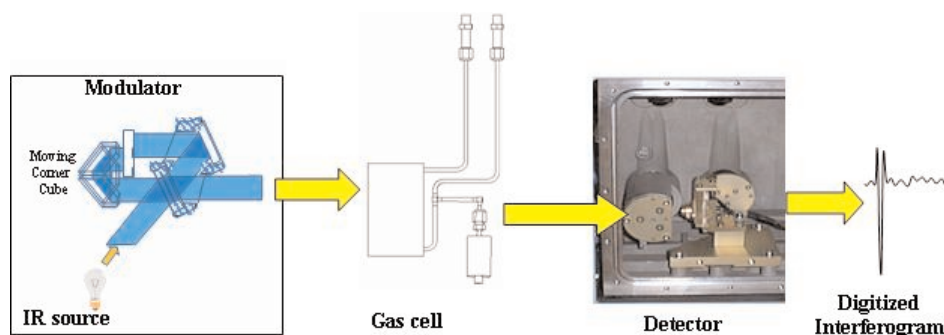
Figure 4.   FTIR Schematic

Figure 5 shows a schematic of how the digitized raw signal or Interferogram is converted to a frequency response signal by performing a mathematical Fast Fourier Transform (FFT). This frequency response signal is eventually converted to an Absorbance signal that is directly proportional to the concentration of the each of the IR active molecules that are present during the time of sampling. In the process shown below, the Interferogram is converted via the FFT to a Single Beam spectrum which produces a signal that is easier to see all of the response

of the IR active components within the gas sample as well as the response of the FTIR instrument. To remove the FTIR instrument response, a non-IR absorbing gas (typically N_2) in passed through the gas cell prior to flowing the sample gas. An Interferogram of the system response as it performs with no sample gas around is collected and stored on the computer. This background response is then used during the sampling process to remove the instrument response from the sample gas signal response. This is accomplished by taking a ratio of the gas sample Single Beam to the instrument background Single Beam. The result is then further processed by taking a negative log of that signal converting the response into the final Absorbance signal which contains all of the responses of compounds in the gas sample that are IR active. The Absorbance spectrum is used as any change in the height of any one of the peaks can be directly related to a change in that components concentration. In order to increase the long term stability of the signal that is produced, the background spectrum is typically replaced every 24 hours.
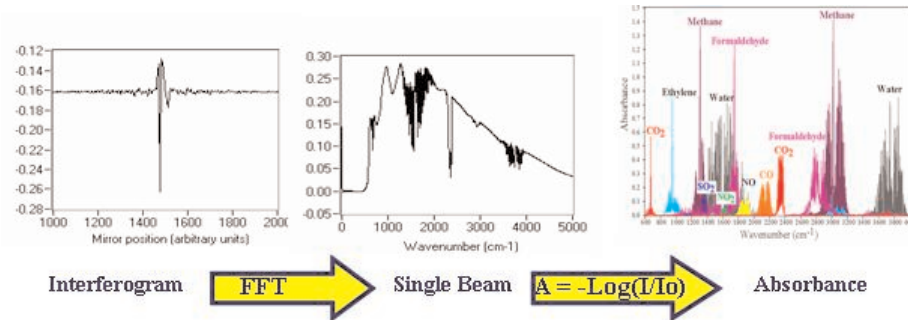

Figure 5.   Interferogram Conversion to Fast Fourier Transform

3.4.4   Cross Interference

Both the GFC and the FTIR are quite resistant to cross interference issues. Due to their multi-component properties, these devices are able to measure and compensate for most cross interference issues directly. In the FTIR methodology the interferences between the various gas phase components can be removed in the software that is used to analyze the data. Unlike NDIR a large number of wavelengths can be scanned at one time and then a software model is made that can distinguish between each of the components that are to be monitored. In general up to about 30 molecules can be monitored at one time in a 1 second time period. Some instruments can handle up to 20 molecules at a 20 millisecond acquisition rate, but in general this fast of a response is not needed for stack monitoring or process monitoring. With the use of more wavelengths as well as a software analysis method, the use of an FTIR leads to a more accurate and reliable measurement of all components at the same instant in time.

3.4.5   Sample Handling

In general, NH_3 is a very water soluble compound, and readily forms salts at lower temperatures. As is the case of any extractive method system (TDLAs, Chemiluminescene and UV-VIS included) the potential formation of salts makes the task of sample handling more challenging and critical to the success of the NH_3 measurement system. Every effort should be made to keep the sample line and probe as hot as possible from the point at which the gas is sampled all the way to the exist of the gas sample cell. Sample probes should be equipped with heated heads and the sample line should be capable of maintaining temperatures above near to or above 180^oC. Careful installation of the sample line to ensure no sags is crucial. Once the gas enters the analyzer cabinet, a heated pump and heated filters are used to avoid "cold spots". In many cases, hot/wet cells (such as the one shown in Figure 6) are designed to operate at high temperatures ($>180^oC$) which limits the amount of NH_3 salt formation that might occur when SO_3 is present as the initial salt formation occurs in the range of 165^oC to 180^oC the temperature is directly related to SO_3 concentration.

However with that said the NH_3 is extremely soluble in water and by keeping the sample gas heated above 180^oC it remain in the gas phase and the formation of Ammonium bisulfate and other salts can be suppressed. The gas sample cell should be of sufficient design as to not warp or degrade under the strain of these high temperature process conditions. Concave mirrors are available in most cases to increase the effective path length (up to 20m) of the IR light path, while maintaining a small internal volume.
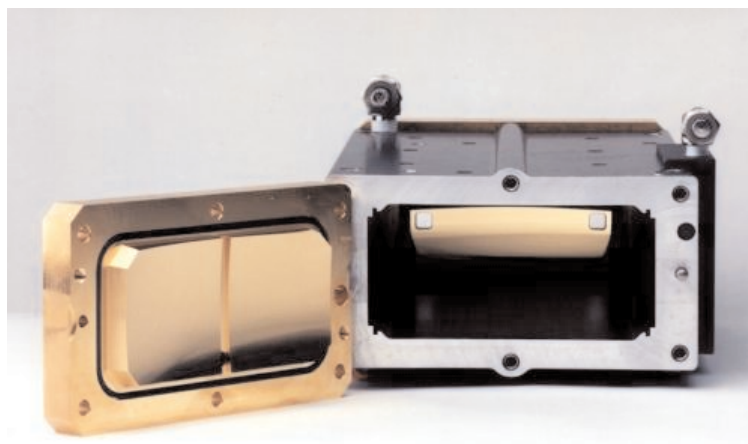
Figure 6.   Hot/Wet Cell

3.4.6   Measurement Locations

Typically, NH_3 is measured in two places in a combustion process. For process control the mea-surement is normally made at the outlet of a NO_x control system, such as an SCR (Selective Catalytic Reduction) or SNCR (Selective Non-Catalytic Reduction) or on the stack as part of a continuous emission monitor (CEM) system.

The measurement of NH_3 is performed at the process control location is to determine the amount of "slip" that is escaping from the reaction process. The SCR is usually located near the end of the process, prior to a FGD or the stack. For the SNCR process NH_3 is typically injected directly into the boiler. Excess NH_3 slip can be a problem for several reasons. The main reason is to optimize the SCR/SNCR process to reduce cost which can increase due to overuse of NH_3 as well as the fouling of fly ash that may be sold off after removal. High levels of NH_3 can also lead to corrosion and maintenance issues further in the process, such as air exchangers, etc.

At the stack NH_3 measurement are made to ensure that the effluent being released conforms to the maximum allowable release levels as defined by the EPA as part of a CEM system. In general, NH_3 is not a commonly regulated gas in the United States, however that is beginning to change as more states as well as and certain industries begin to require NH_3 monitoring.

The measurement sensitivity is dependant upon the measuring path length and the opaqueness (particulate matter density) of the gas stream Measurements are performed using the extractive sampling technique that draws a sample stream from across the stack or duct then transports it via heated lines, filters and pumps to the analysis equipment. Various configurations can be chosen to define the process interface by the choice of gas cell pathlength and volume, IR detector, sampling and gas cell materials, purging modes, in order to adapt the sensors for process engineering mea-surements or as a CEM measurement.

Due to the multi-component nature of both the NDIR and FTIR analyzers, their benefits typically lie in the CEM application at the stack location, where NH_3 can be easily added to a system analysis method which may already include regulated gases such as SO_2, NO_x, CO, HCl, hydrocarbons and others.

3.4.7   Minimum Detection Limits

For both the NDIR analyzers as well as the FTIR analyzer, the minimum detection limits are based up on the actual system configuration. In the case of the NDIR they have a typical minimum range in the area of 0-30 ppmv with a detection limit of 2% of full scale or 0.6ppmv.

FTIR analyzers, like the Laser Diode systems, have sensitivity and minimum detection limits based upon each component which are path length dependent. The longer the path length, the higher the absorption and the higher the sensitivity which equates to a lower detection limit. Therefore, longer path lengths gas cells result in better detectability of low concentrations. The FTIR is also capable of providing accurate measurement spanning concentrations ranging from ppbv (parts per billion – volume) up to percent for most of the typical components present in a CEM stack using the same system.

Dust loading in the effluent stream needs to be filtered out within the heated extractive sampling system prior to entering the gas cell of the FTIR. Dust eventually does penetrate to the gas cell mirror reducing the overall light that reaches the detector. Because the FTIR uses a reference background to remove system "noise" it is able to tolerate up to a 40% loss in the overall signal without affecting the accuracy of the measurement.

During a preventive maintenance schedule the gas cell as well as the mirrors can be easily removed, cleaned and reinstalled by the end user without requiring the system to be realigned.

Water vapor is particularly active in the IR spectral region and it must be taken into consideration when creating a method for the analysis in both the NDIR and FTIR techniques. In the case of NDIR the filter region is chosen so that it avoids the regions that have a strong water signal. In the case of FTIR interference from the water vapor signal can be reduced by the development of algorithms that either mask or remove this interference.

Detection limits (based upon 2 Standard Deviations about the mean value when N_2 is flowing through the gas cell) for NH_3 using FTIR on coal fired boilers dependant on the above criteria are achievable at the 0.2 ppmv level. In this particular instance a 5 meter (m) path length gas cell at 191^oC in the presence of up to 40% moisture and using $0.5cm^{-1}$ resolution was use. Because the FTIR signal can be acquired in the presence of high moisture levels, a chiller is not needed and the amount of NH_3 that is in the effluent gas stream can be obtained directly.

3.4.8   Calibration Requirements

For both NDIR and FTIR permanent calibrations are made on the initial instrument (they can be provided by the instrument manufacturer directly). Ammonia calibrations are created using the standard EPA single component calibration technique. The standards will need to be created using a NIST certified permeation tube system that requires tightly controlled heater ovens and at least two mass flow controllers (MFCs) to blend the starting concentration down from 100 ppm to 1 ppm. The assumption is that below 1 ppm the system response will be linear.

The system performance can be periodically checked by running a certified gas standard at the analyzer ensuring that the system is still performing accurately. Some instrument companies have internal validation standards that can be run.

During a Relative Accuracy Test Audit (RATA) performance test both the NDIR and FTIR are validated via a certified caibration gas standard spike injected into the system at the probe, which allows for a full check of the entire sample system. The method can be validated by running a sample of the calibration gas at the inlet of the NDIR or FTIR. Additionally, many NDIR systems are available with internal filter calibrations, which eliminate the need for gas bottles.

3.4.9   Maintenance Requirements

Typical maintenance procedures for extractive sample systems apply which generally includes maintenance on the pumps, replacing filters, cleaning sample probe and heated lines. For the FTIR and NDIR units themselves, the window on the gas sample cell made need to be cleaned or replaced if the light throughput decreases below 40% of the starting value. The mirrors of the FTIR gas cell will also need to be removed and cleaned.

In the case of the FTIR some manufactures will require periodic IR light source replacement on a 1-2 year average while others may require a laser light source replacement on a 3-4 year time base. For either light source, the analyzer should monitor the current required to power the unit as a function of aging and let the end user know, in a preventative way, when the light source needs to be replaced.

3.5 UV Spectroscopy

UV Photometry is a well known technique for measurement of NH_3, and many other UV absorbing gases such as NO, NO_2, and SO_2. It is utilized in both extractive and in-situ (both point and cross duct) monitoring concepts. The principle of operation is detection of gas absorption in the UV spectrum, typically from 200nm to 250nm.

3.5.1   Detection Techniques

The detection and signal evaluation principle of the Non-dispersive untra-violet (NDUV) technique with Interference Filter Correlation (IFC) is often used for NH_3 applications. In this technique, interference filters with different transmission characteristics are swung successively into the light path. These interference filters are used to determine the background absorption from other UV absorbing gases, mitigating the effects of cross interference. A standard solid state detector is typically used in these devices. The absorption response of the analyzer is then compared to a calibration curve, stored in the units internal memory during initial calibration to determine the concentration of the gas component.

Differential Optical Absorption Spectroscopy (DOAS) is also utilized as a standard detection technique. This detection is accomplished by a 256 photodiode array, with each diode possessing a spectral range of about 0.11 nm. Using a technique called Holographic grating, each diode will be exposed to a light value after absorption by the sample gas. With the advent of photodiode array detectors, the DOAS principle has become a more commonly used techniques for measurement of trace compounds, such as NH_3. To perform a DOAS measurement, two spectrum must be measured. One, called the reference, where the UV light passes through little (or no) absorptive gas.
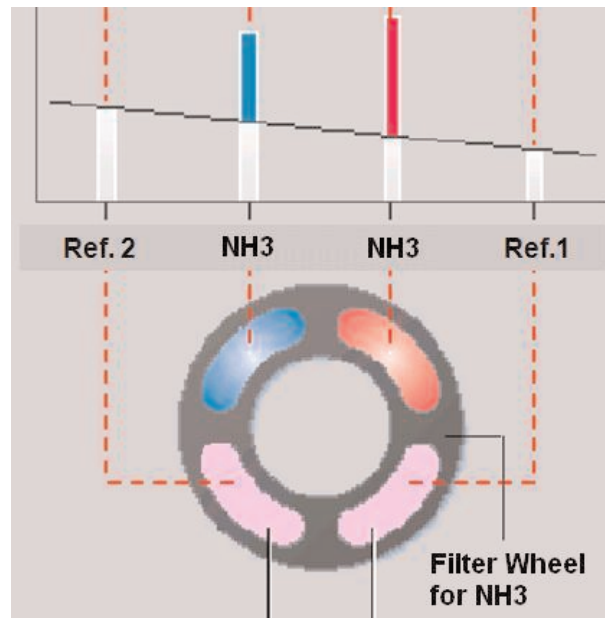
Figure 7. Filter Wheel for Ammonia

They other, called the measurement, is passed through a cell containing the gas to be measured. By comparing the reference to the measurement spectrum, an absolute absorption curve can be determine and compared to other spectra stored in the analyzers internal memory during calibration. Because the absorption spectrum is compared to fixed calibration spectrum, this type of UV detector is very stable, offering long term operation with little to no drift.

3.5.2   Cross Interference

Because many other components absorb in the UV, cross sensitivity can be an issue. In particular SO_2 is of interest, as it absorbs cross a wide band of the UV spectrum. High background levels of SO_2 can be a limiting factor as to the lower detection limits of some UV devices, due to masking of the NH_3 absorption peak. IFC system can be less susceptible to SO_2 cross interference than DOAS systems due to the interference filters effect. However, in the case of DOAS analyzers, where the background SO_2 is known at the time of calibration, many of these effects can be compensated for.
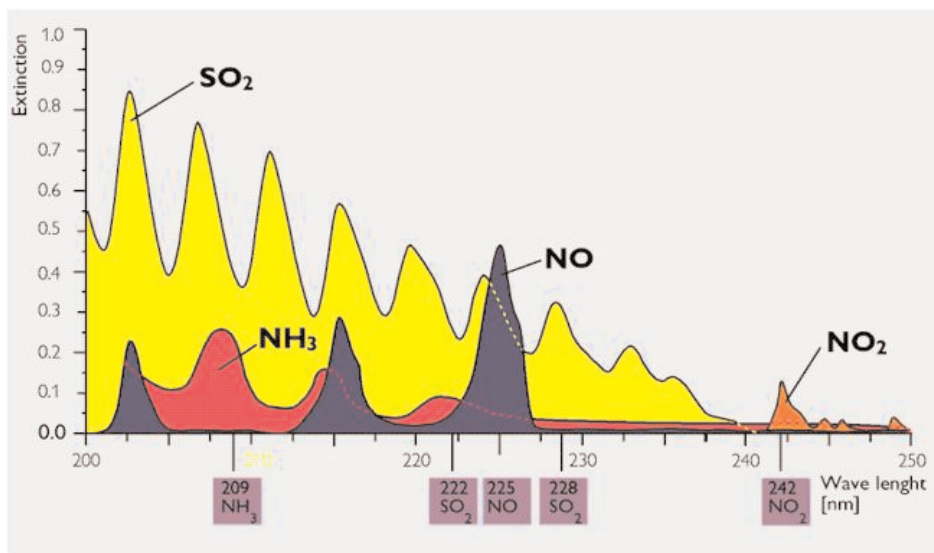

Figure 8. UV Spectrum of SO_2, NO_x and NH_3 Absorption

While H_2O presents as a strong cross interference culprit in NDIR and FTIR detection analyzers, it absorbs universally in the UV spectrum. This leads to a consistent offset that can be compensated for in the analyzer electronics, thus having no effect on the NH_3 measurement.

3.5.3   Sample Handling

In general, NH_3 is a very water soluble compound and can readily form salts at lower temperatures. This makes the task of sample handling very difficult if the process is not in situ. Extractive systems can face distinct problems related to NH_3 loss in the sample handling system due to both salt formations and as well as it will drop out with the water if a chiller is used. Therefore sample probes should be equipped with heated heads and the sample line should be capable of maintaining temperatures above near to or above 180°C. Careful installation of the sample line to ensure no sags is crucial. Once the gas enters the analyzer cabinet, a heated pump and heated filters are used to avoid "cold spots". In many cases, hot/wet cells (such as the one shown in Figure 6) are designed to operate at high temperatures (>180 °C) which limits the amount of NH_3 salt formation that might occur when SO_3 is present as the initial salt formation occurs in the range of 165 °C to 180 °C the temperature, is directly related to SO_3 concentration. However with that said, the NH_3 is extremely soluble in water and by keeping the sample gas heated above 180 °C the NH_3 will remain in the gas phase and the formation of Ammonium bisulfate is suppressed.

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At the stack NH_3 measurement are made to ensure that the effluent being released conforms to the maximum allowable release levels as defined by the EPA as part of a CEM system. In general, NH_3 is not a commonly regulated gas in the United States, however that is beginning to change as more states as well as and certain industries begin to require NH_3 monitoring.

3.5.5   Minimum Detection Limits

Minimum ranges for both IFC and DOAS type UV analyzers are near the upper limit for use in SCR/SNCR slip applications. Typically, a minimum range of 0-50/75 ppm is found. Accuracy at these ranges is +/- 2% a detection limit using a 2 standard deviation value of 1.0 ppm for the 0 – 50 ppm range.

3.5.6   Calibration Requirements

Both IFC and DOAS type UV analyzers can be calibrated using either a certified calibration standard injected at the inlet to the analyzer or by the use of internally mounted optical filters. To test the sampling system a calibrated gas standard is injected at the probe. In process applications, the use of internal filters can substantially reduce the customer cost for calibration gas, reducing cost of ownership. In certain EPA applications (40 CFR Part 60) this is also the case.

3.5.7   Maintenance Requirements

Outside of the standard maintenance required of any extractive systems (pump rebuild, filter changing, etc.) the main maintenance requirement of any UV measurement system, extractive or in-situ, is replacement of the light source. For most IFC extractive systems, replacement of the UV light source should need to occur no less than every 2 years. For a DOAS in-situ type device, which by its nature sees much harsher conditions, a light source should last for 12-18 months. The analyzer should monitor the current required to power the lamp as a function of aging and let the end user know, in a preventative way, when the light source needs to be changed.

Filters in the in-situ probe may be cleaned at an interval that is typically site specific. Many in-situ UV analyzers have been installed in post SCR applications, and have run for 2-3 years without the probe filters being cleaned. This means the maintenance requirement on these types of analyzers is limited to replacement of the light source. Light source replacement usually takes 30 minutes or less.

4.0 CONCLUSIONS

Continuous ammonia monitoring technology is available for all types of combustion systems equipped with SCR and SNCR NO_x control systems. There are several technologies available that can be placed directly into the stack or which use extractive techniques to bring the sample from the stack to the analyzer. Some require little or no pretreatment while others require more extensive pretreatment which may compromise the NH_3 content with in the stream so care must be taken to ensure the NH_3 stays with the gas stream.

4.1 Value of Monitoring Ammonia

Ammonia is an undesirable pollutant that can result from NO_x control systems. Monitoring ammonia emissions from NO_x control systems ensures NH_3 is controlled to low levels.

Aside from monitoring stack emissions, measuring ammonia slip on a continuous basis is very beneficial to getting the most out of NO_x reduction equipment. Important benefits of using ammonia monitoring include the early identification of NO_x control system malfunctions – this will help avoid the following problems:

- Avoiding plugging of the air heater and the associated unplanned outages – unplanned outages can cost a power plant hundreds of thousands of dollars every day it is out of service.
- Avoiding high ammonia levels in fly ash that can cause fly ash disposal issues and personnel hazards – if fly ash is "smelly", it can be difficult to find companies that will accept it for disposal because the odor can create a personnel hazard.
- Ability to increase the plant NO_x reduction and selling the excess NO_x allowances – under a NO_x trading regime, it is possible to over control the SCR while monitoring and maintaining ammonia slip low to generate allowances for sale.
- Economic benefit of optimizing chemical injection to reduce consumption of NH_3 and urea.
- Improve and extend catalysis life cycles.

4.2 Future Emissions Monitoring Requirements

In addition to process monitoring applications, the past 2-3 years have seen and increase in NH_3 monitoring requirements through permits. Many newly built plants over this time frame, have seen the analysis of ammonia written into there permits. Even existing plants, particularly in the Nitric Acid and Cement industries have seen these permit changes. Industry should expect these requirements to continue, especially as EPA focuses on $PM_{2.5}$. NH_3 has been designated as a precursor for $PM_{2.5}$, and thus will be considered as a surrogate measurement to predict PM fine emissions.

As discussed, there is not a dedicated Performance Specification for monitoring NH_3. This has given individual plants some flexibility in how they monitor NH_3, and allows for some open discussion with local regulatory officials regarding QA/QC requirements. In general, the NH_3 monitor will be required to meet the requirements of 40 C.F.R. Part 60, App. B and F, including Performance Specification 6. EPA Conditional Test Method, CTM-027: Procedure for Collection and Analysis of Ammonia in Stationary Sources, has been sited as reference method.

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