Environmental awareness for clean air becomes more important each passing year, especially when measuring nitric oxide (NO) and nitrogen dioxide (NO₂) in stack emissions. Regulations require reporting stack NOₓ as a combination of all oxides of nitrogen. NO and NO₂ are distinct measurements that can add up to report total NOₓ. And with environmental awareness comes more stringent demands on NOₓ measurement for lower ranges. Several methods of measuring NOₓ have proven effective over the years, but a more effective way to measure stack emissions is to use a single photometric analyzer for simultaneous measurements of NO and NO₂.

The emissions found in exhaust gases from combustion processes contain parts-per-million (ppm) levels of NO and other oxides of nitrogen, primarily NO₂. The Clean Air Act of 1970 and its 1990 amendments emphasized the measurement of NOₓ.

It is typical to analyze only the NO component directly, catalytically converting the other nitrogen oxide species to NO and analyzing them as total NOₓ. With several methods to choose from in measuring NOₓ, the most common is chemiluminescent. But there are maintenance issues involved and scheduled catalysts.

The U.S. has traditionally used a molybdenum converter, measuring either with infrared or chemiluminescent methods. With the higher levels of NO and NO₂, infrared can be effective, but on lower levels, ultraviolet adds accuracy. Most sources required 0-10 or 0-20 ppm, which leaves infrared ineffective and leaves the choice of chemiluminescent or ultraviolet.

**Ultraviolet proves effective**
An ultraviolet analyzer provides multi-component measurement capability for simultaneous measurement of NO and NO\textsubscript{2} as well as sulfur dioxide (SO\textsubscript{2}). Modern processing adds the discrete measured values for each component to report total NO\textsubscript{x}. Separate measurements of NO and NO\textsubscript{2} eliminate any need for the traditional converters that have seen frequent use. Using ultraviolet minimizes several maintenance issues. With ultraviolet, there is no converter and no need to use a chemiluminescent type of analyzer. Using a UV analyzer in real time gives the user a view of NO\textsubscript{2} and NO without the converter.

The U.S. EPA has amended reference method 7E to accept the use of UV-based photometers as an instrument test method. Differential ultraviolet, resonance absorption spectroscopy (DUV-RAS) analyzers are low in noise and reduce costs. Plus, water and carbon dioxide do not interfere with measurements.

**Differential ultraviolet technique**

The UV radiation source for a DUV-RAS analyzer is a special electrodeless discharge lamp as the UV radiation source. The source is filled with a combination of nitrogen (N\textsubscript{2}) and oxygen (O\textsubscript{2}).

A high-frequency circuit induces the formation of plasma within the source. The N\textsubscript{2} and O\textsubscript{2} disassociate in the plasma to form excited NO. UV light emits as the electrons in the plasma drop from the excited state to the molecules’ ground state at a wavelength of about 226 nm. This wavelength is isolated for use to measure NO by means of an interference filter. The reactions taking place in the plasma for this purpose may represent in simplified form as in the following equations:

\[
\begin{align*}
O\textsubscript{2} & \rightarrow O + O \\
N\textsubscript{2} & \rightarrow N + N \\
N + O & \rightarrow NO^* \\
NO^* & \rightarrow NO + h\nu \\
2 NO & \rightarrow N\textsubscript{2} + O\textsubscript{2}
\end{align*}
\]

Where: \( h\nu = \text{NO specific resonance-radiation (RAS)} \)

The NO molecule in the excited state will have numerous different rotation-vibrational states, which can release UV radiation. The energy released from these states produces a characteristic set of emission lines specific to NO at the 226 nm wavelength. Some of these lines consist of “cold” lines that NO can absorb in sample cell and that we can consider measuring radiation. Another part of the lines consist of “hot” lines (energy not absorbed by NO molecules) and pass unaffected to a detector. We can treat these lines as reference radiation.

**Analyzer design**

The complete radiation from the source for the NO band at 226 nm is helpful in measuring radiation wavelength. Measuring radiation then is the sum of “cold” and “hot” lines. The hot lines along with the corresponding wavelengths are reference radiation in the DUV-RAS method. In addition to the hot and cold lines, a second mechanism provides measurement reference for the analyzer. This mechanism consists of a beam splitter, which separates the UV radiation and directs it to a reference detector and through a sample cell to a measurement detector.

A separation of cold lines and hot lines at 226 nm takes place by a gas filter located on a filter wheel, which fills with a defined NO concentration.
The combination of the effects from hot lines and cold lines separated on a time basis with the beam split to reference and measurement detectors is called a four-beam optical method. There are four intensity measurements: \( R_1, R_2, M_1, \) and \( M_2 \). \( R_1 \) is the measurement of the source intensity when the filter wheel is open. \( R_2 \) is the measurement of source intensity when the filter wheel contains a sealed cell with NO, thus blocking specific NO wavelengths. \( M_1 \) is the intensity of the source minus that absorbed by gas in the sample cell. \( M_2 \) is the intensity of the source minus that absorbed by the NO gas filter and nonspecific absorbance in the sample cell. \( M_1 \) and \( M_2 \) separate in time, as do \( R_1 \) and \( R_2 \). The absorbance, which only the measured component (NO) in the sample cell causes, is:

\[
A = \frac{\frac{R_1}{M_1} - \frac{R_2}{M_2}}{\frac{R_1}{M_1}}
\]

**NO\textsubscript{2} component measurement**

The analyzer provides additional measurement of NO\textsubscript{2} as a second measured component by the wavelength correlation method. Measurement wavelength is at 400 nm and reference wavelength 580 nm. Wavelength filters are fitted to a filter wheel and positioned on an alternate time basis corresponding to the timing for the NO component described above. Information is provided in sequence for the NO\textsubscript{2} and the NO components. No other exhaust gas component absorbs in this range, so NO\textsubscript{2} can be measured without cross interference.

You can select multiple wavelengths with the correlation technique that allows the additional capability for measuring SO\textsubscript{2}. Additional wavelengths selected fit to the filter wheel, again positioned on a timed sequential basis at the measurement wavelength for SO\textsubscript{2} of about 268 nm.

**Calibration**

The calibration of analyzers generally includes introducing cylinder calibration gases. This describes the capability to calibrate without a flowing gas. A calibration wheel contains gas-filled cells, that when moved into the optical path are equivalent to an absorbing gas in the sample cell and are suitable for span calibration or validation. During calibration procedures, the sample cell fills with nitrogen zero gas to establish a stable baseline. \( N_2 \) also provides the reference for zero point calibration.

The calibration cells for NO fill with a NO/N\textsubscript{2} mixture of a known
concentration. An analyzer that measures separately NO and NO\textsubscript{2} require multiple gas cylinders. Interactions between the two NO\textsubscript{x} species in a single gas mixture cylinder or in sample conditioning might introduce procedure errors in calibration.

The NO\textsubscript{2} calibration gas in particular is difficult to handle. Stability of the component in a pressure cylinder is suspect, and handling of NO\textsubscript{2} in a sample path can be difficult. We compared the stability of the NO\textsubscript{2} sample cell with stability of NO\textsubscript{2} in a cylinder gas; the test duration was about nine months. We analyzed the NO\textsubscript{2} test gas cylinder at the beginning and end of the test.

Response correlations

Several investigators have evaluated the performance of NO\textsubscript{x} analyzers. These referenced test procedures compared analyzers using chemiluminescent, infrared, and DUV-RAS (NDUV). Tests evaluated analyzer performance such as stability, calibration repeatability, and response to interference. Equipment configurations in these examples all included the analyzer with NO\textsubscript{x} converters.

Sample handling designs in all cases were similar for both compared units. Test samples consisted of exhaust vapors that sample bags captured and transported to the analyzer for evaluation. Investigators calibrated both analyzers on the same gases and introduced the same samples for each data set reported.

The converter efficiencies reported >98% for this first example. A good linear relationship exists for all the data. On average, the chemiluminescence detection (CLD) shows 5% lower NO\textsubscript{x} values compared to the UV-RAS NO\textsubscript{x} results. Some have attributed this to a probable quenching effect found in the CLD analyzer.

The data of the CLD and the UV-RAS NO/NO\textsubscript{2} analyzer also have good correlation. Again the CLD data is consistently 5% lower compared to the NO/NO\textsubscript{2} analyzer.

Signal quenching

The likely cause for the CLD results consistently showing 5% less than UV is a quenching effect on the signal caused by CO\textsubscript{2} and water vapor in the tested sample. Basic technology of the CLD analyzer is a light-producing reaction in a sample chamber where a flow of sample containing NO mixes with ozone (O\textsubscript{3}). As NO and O\textsubscript{3} mix in the reaction chamber, the chemiluminescent reaction produces light emission directly proportional to the concentration of NO. Measure this emission with a photo-multiplier tube and associated electronic circuitry. Quenching is an effect that may result when molecules in the sample composition absorb some of that light emission before it can reach the detector. The flue gas composition contains CO\textsubscript{2} and H\textsubscript{2}O that may enter into the quenching process in the CLD analyzer. This process is called quenching because the light is quenched or reduced. Yet in order for quenching to occur, NO must be present in the measured sample; if NO is not there to
react with $O_3$ to form light, there is no light to be quenched.

Testing of several analyzers with NO present in the sample shows a strong quenching effect in some of the units. CLD analyzers showed response to $CO_2$ concentration to varying degrees. The UV demonstrated no effect as $CO_2$ concentrations increased.

**NO$_x$ converter**

Using traditional methods of measuring oxides of nitrogen involving CLD, UV, or IR requires a catalyst based NO$_2$ to NO converter. The NO$_x$ converter introduces factors that could cause variability in the measurement. Parallel analysis of both NO and NO$_2$ eliminates the need for a converter and reduces potential problems the converter may cause.

You can use several different catalysts in the NO$_x$ converter, including molybdenum, molybdate-carbon, vitreous carbon, and stainless steel. You could select any of these catalysts for NO$_x$ conversion based on design and operational parameters, and each catalyst will function with efficiency, but never at 100%.

The catalysts tend to drop in conversion efficiency as they age, and at different rates. In order to characterize total NO$_x$ precisely, you must know conversion efficiency at any given time. Variability in efficiency yields variability in NO$_x$ measurement output.

Catalysts will also age at a rate proportional to the NO$_2$ content of the sample. NO$_2$ content in stack NO$_x$ has appeared in higher ratios than previously expected—in the NO to NO$_2$ neighborhood of 70/30. Efficiencies drop more quickly in this case.

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**RESOURCES**

- It’s the law; now what? [www.isa.org/InTech/20080504](http://www.isa.org/InTech/20080504)
- Monitoring NO$_x$ emissions [www.isa.org/link/nlox2005](http://www.isa.org/link/nlox2005)