The On-Line Detection of Oxides of Nitrogen in Light Hydrocarbon Streams by Modified Chemiluminescence Detection and/or by Dry Colorimetric Detection

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Abstract:

Producers of high purity monomers (ethylene) have identified the need to measure the presence of Oxides of Nitrogen (NOX) at very low PPB levels, and take steps to avoid potentially hazardous conditions, in the Cold Box.

NOX (NO and NO_2) in the olefins processing train is a safety concern. There is a possibility of accumulation of unstable liquid or solid nitrogen oxide ($N2O_3$) and nitrogen oxide-organic solids in the cold processing equipment.

In the Cold Box of ethylene production plant at temperature, 130 C to 170 C, oxides of nitrogen may combine with dienes (gums) and form potentially explosive nitrated resins.

During, shut down, at the time the olefins recovery train is allowed to warm up, any cracked gas flow passing through sections where N_2O_3 has deposited, will lead to the formation of extremely hazardous conditions. This is due to the reaction of NO_2 and N_2O_4 with heavier olefinic materials. The NO_2 can react with olefinic materials to form "gums". These 'gums' formed are explosive at cryogenic temperatures. NOX deposits represent the presence of a powerful oxidizer in a system filled with flammable materials.

Even though, in theory, Nitric Oxide ('NO') is the only NOx species that reaches the cryogenic ethylene recovery unit, it is also required to measure other species that belong to NOX group.

If NOX levels are below five parts per billion in the cracked gas, then accumulations would not be expected to occur. However, if the concentration is over 30 ppb, accumulations in one form or another are assured.

The analytical challenge of NOx in Light Hydrocarbons Analysis:

The measurement of 1 ppb-50 ppb levels of NO in complex olefins matrixes is a major analytical challenge. The detection is required at 1 PPB level. This is difficult due to the presence of major interference of the matrix and trace level contaminants at PPM levels.

Many analytical techniques fail in this application, including GC-Chemiluminescence and GC-PID due to lack of the required sensitivity or specificity.

C.I. Analytics has solved this analytical problem using two different detectors. One is Dry Colorimetery Detector and the other is the modified GC-Chemiluminescence.

In the past, several efforts have been made to detect NO using Gas Chromatography followed by detection using either a Photo ionization detector or traditional chemiluminescence detector. Both these detectors require accurate gas chromatography work and slight variation in retention time will result in false results.

The PID can detect down to 80 PPB. The GC-Chemiluminescence (traditional detector) is not truly applicable to on-line work, while experienced chemists have made detections at 50 PPB level. This does not meet the analytical requirements of measuring NOX at levels much below 50 PPB.

The new modified chemiluminescence detector by C.I. Analytics and another field proven technique, Dry Colorimetery method to detect NO provides a successful technical solution to this analytical problem.

Current Detection Techniques

A Case Study with GC-PID or GC-Chemiluminescence:

Take as a case study the detection of one impurity:
Nitric Oxide in Ethylene.

Detection of nitric oxide in ethylene, propylene, or 1, 3 butadiene is very difficult at the desired 1 ppb level. Normally, a complicated GC column system is used to separate nitric oxide from propylene. After this separation of low ppb levels of the impurity from almost 99.9% ethylene and other ppb or ppm levels of other impurities, such as hydrogen cyanide, nitric oxide, ammonia, or hydrogen chloride. This being the case, with many other impurities present at low ppb levels, it is easy to misidentify the NO peak. Thus, the individual working with GC-PID must be highly skilled. Even the most experienced chemists experience difficulty in positively identifying and accurately quantifying low (1-10 ppb) levels of this impurity. As a result, most companies have stopped using this technique for NO detection.

The laboratory technique, the GC-Chemiluminescence or GC-PID technique for ppb-level NO detection is only available for laboratory testing applications to date. Further, both of these techniques are not only impractical for on-line applications, but they are also very expensive to install and maintain. It is clear that, in today's monomer-production facilities, non-specialist technicians must be able to quickly, efficiently, and accurately perform NO analysis without GC separations both either in the lab or on-line.

Using Modified GC-Chemiluminescence.

The traditional Chemiluminescence detector, for the detection of 1 PPB levels of NO requires reaction of NO with Ozone at reduced pressure. That means there is a need for the use of a vacuum pump. This pump will create reduced pressure in the reaction cell of the detector. The detector response will change as the vacuum conditions change. Plus, vacuum at the end of GC column leads to retention time problems. If retention time is shifted, then false results will be reported. Not to mention total failure if ethylene reaches the detector, as ethylene will give a big response (false peak).

The GC-Chemiluminescence detector responds to PPB levels of ethylene. So, the choice of the GC-columns is extremely important. Two conditions must be observed. First, the analytical column must separate NO from ethylene. Second, the complete system must be inert. The columns, valve, loop and connective tubing must not adsorb NO at low levels.

All these factors have made on-line detection of NO very difficult, even though, in some labs, good results at 50 PPB level have been achieved.

C.I. Analytics has solved this problem. The need for use of vacuum pump has been eliminated. The analytical system is made inert; the photomultiplier tube has been replaced by another photo sensitive device. The problems associated with interferences have been reduced. The ethylene at PPM levels will not interfere. The GC Columns are packed 1/8 inch and the detector is sensitive down to 1 PPB level of NO.

Using Dry Colorimetery Detection for 1 PPB level NOx.

The GC-Chemiluminescence detection requires more attention than the on-line service teams has the time to devote. Is there another technique that will give accurate results without the need for special care? In addition, it is desired for complete safety and prevention of explosive resins, that Total NOx be measured and reported instead of assuming that only NO will reach the cold box.

It is at this point that the time-proven analytical technique of Dry Colorimetery draws new attention. The application of the dry colorimetric technique to the measurement of trace NOx in the hydrocarbon streams has been independently demonstrated by several petroleum/petrochemical companies. Figure 1 indicates potential monitoring points in an olefin/polyolefin plant for trace NO measurements. With prompt, reliable on-line results, the

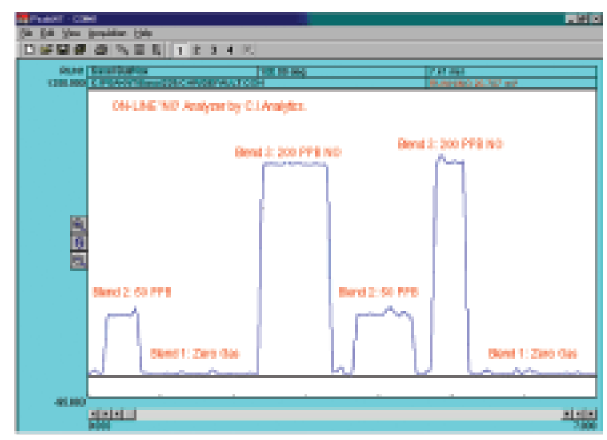


Figure 1: CI Analytics On-Line NO Analyzer
C.I. Analytics: GC-Chemi for 20 PPB NO detection at customer location since the year 2000.

process control engineer has the opportunity to develop strategies to minimize the formation of potentially explosive nitrate resins in the cold box. The results obtained using Dry Colorimetery technology corresponded to the laboratory results, using GC-chemiluminescence, within experimental error.

C.I. Analytics has developed a special formula that is deposited on the filter tape. This tape will respond only to NOx.

A New Look at Dry Colorimetery:

Introduction

Classical Colorimetery utilizes an impinger to collect gas in a liquid medium. Chemical reagents are then added to the medium to cause it to change color in proportion to the concentration of gas present. The resulting color change is measured by a laboratory spectrophotometer and compared to known standards.

Ultra-sensitive "tape" detectors are also colorimetric based, but these are dry reaction substrates that serve as gas collecting and analyzing media. Individually formulated for a specific gas or family of gases, each detection tape is a non-toxic, proprietary chemical reagent system. When exposed to a target gas, the tape will change color in proportion to the amount of gas: the higher the target gas concentration, the darker the stain that will appear.

The change in color, or stain, on the tape is read by a photo-optical system in the analysis instrument, and the intensity of this stain is then compared to a standard response curve pre-programmed into the instrument's data system.

Analytical Technique

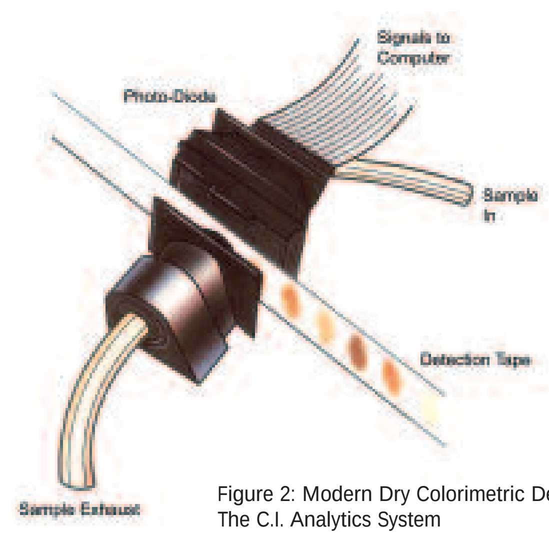


Figure 2: Modern Dry Colorimetric Detection:
The C.I. Analytics System

During operation, the detection tape is incremented through a sampling "window" where it is exposed to a metered sample stream. If the target gas is present, a stain proportional to the concentration develops. Simultaneously, a beam of light is reflected off the exposed portion of the tape and the intensity of this light is measured continually. As the amount of reflected light decreases due to stain development, the reduction is sensed by a photocell detector as an analog signal. This signal is converted to a digital format, matched to the gas response curve stored in the analyzer's permanent memory, and displayed/ documented as the actual concentration value. All of these functions are microprocessor controlled and, in the best cases, carried out by a complete computer.

The use of this spectrophotometric technique, in combination with microprocessor/complete computer control, provides excellent accuracy, repeatability, and detect-ability of low ppb (parts-per-billion) concentrations.

Accuracy of Dry Colorimetry for NOX Detection.

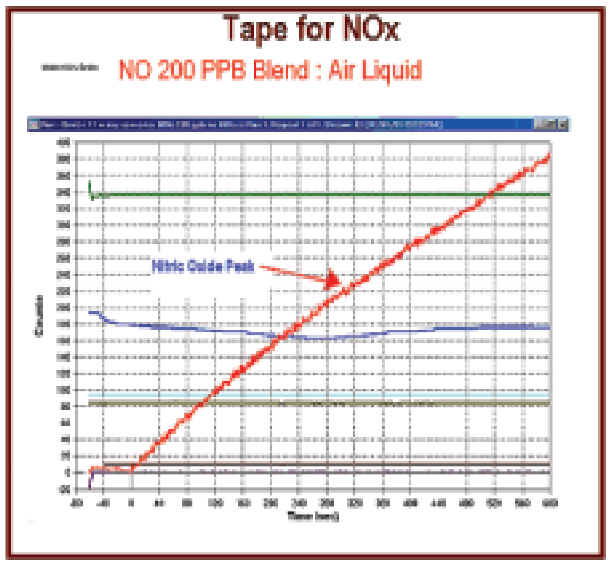
The dry colorimetric detection technique, as outlined above, gives accurate and extremely precise results. Factory calibration of instruments and the detection tape is referenced against NIOSH approved and analytical methods. Both laboratory and field tests have verified that analyzers using Dry Colorimetery give data in agreement with standard reference methods, as typified by the examples in Table 1.

Gas	Concentration as Determined by Standard NIOSH Methods	Analyzer Reading (ppb)
NO2	10	14
	45	47
	100	104
NO plus	200	202
NO2	100	97
	10	6

Table 1: Dry Colorimetric Results as Compared to Those of NIOSH Standard Methods

The graphical analyzer response shown below was obtained by using certified 200 PPB, NO blend from Air Liquid. This blend was diluted to get standards at 10 PPB and 20 PPB.

Figure 3

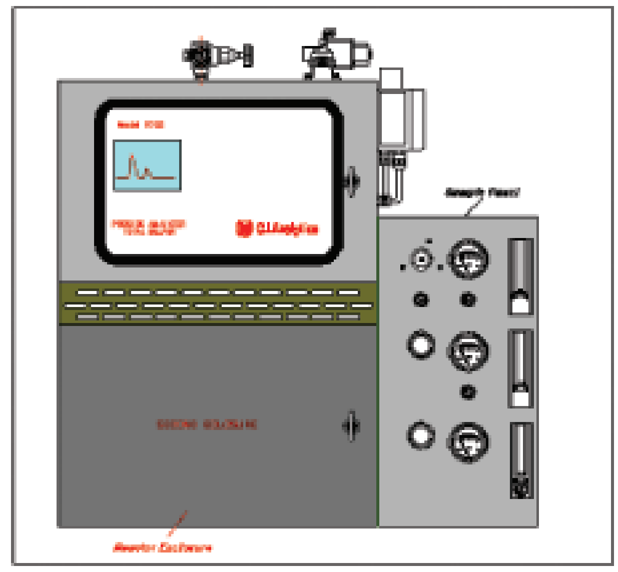


Key Benefits of Dry Colorimetery for NOx Detection in Monomer Production Plants:

It has been established that low-level NOX analysis is of crucial importance for those involved in high-purity monomer production. C. I. Analytics' analyzers operating on Dry Colorimetery that are designed for low-level NOx analysis, offer producers the following key benefits:

• The NOx detection tape reacts instantly to the NOx for fast results that are visible due to the color reaction. For example, it takes less than 90 seconds to detect and measure ppb levels of NOx, without use of any GC columns.
• Dry colorimetric detection is very sensitive, allowing for low-level analysis of NOx family. The NOx must be identified in process streams at ppb levels for subsequent removal.
• Dry Colorimetry is also very specific to the gas that the detection tape is designed to measure. It will not react to other substances (solvents, hydrocarbons, etc.) often found in process streams or other samples. As a result, expensive downtime due to false alarms is virtually eliminated. The NOx Tape is sensitive only to oxides of nitrogen.
•Total NOx result is obtained.
•No need for GC columns or GC specialist.

• There is no Ethylene interference
• unmatched accuracy at ppb levels
• simple to use by non-technical staff:
  o no GC separations and no complicated set ups
  o clear, unambiguous results that require little interpretation: if the instrument operates with a complete computer and proprietary software, the "Peak", as it elutes, can be displayed on the screen, and a numerical concentration value can be viewed
• laboratory or on-line use, depending upon instrument area classification.



Conclusion

Low level NOx analysis, at low ppb levels, is increasingly crucial to ensure the accurate monitoring of NOx and thus reduce the built up of potentially explosive nitrated resins.

Current techniques utilized for such detection are expensive, require a high-level of technical expertise, and are generally highly maintenance intensive.

Gas chromatography with modified chemiluminescence detection provides a successful technical approach to this measurement need. The modified chemiluminescence detector can provide the sensitivity required to measure NO without the need of vacuum pump.

The GC method is limited to NO detection only. For the detection of Total NOx, the new Dry Colorimetery Detector offers a new solution to lab or on-line monitoring. This detector is low in maintenance and easy to work with.