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 NO2) in the olefins processing train is a safety concern. There is a possibility of accumulation of unstable liquid or solid nitrogen oxide (N2O5) and nitrogen oxide-organic solids in the cold processing equipment. In theCold 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 flowing through sections where N2O5 has deposited, will lead to the formation of extremely hazardous conditions. This is due to the reaction of NO2 and N2O5 with heavier olefinic materials. The NO2 can react with olefinic materials to form “gums”. These “gums” form 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 matrices is a major analytical challenge. The detection is required at 1 PPB level. This is difficult due to the presence of major interferences of the matrix and trace level contaminants at ppm levels.

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

C.I. Analytics has solved this analytical problem using two different detectors. One is Dry Colorimetry 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 NO levels much below 50 PPB.

The new modified chemiluminescence detector by C.I. Analytics and another field proven technique, Dry Colorimetry 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. Thus 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 time consuming. It is common 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 Oxide 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 connecting 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 PPB 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 Colorimetry 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 Colorimetry 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
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 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 detectability 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 Colorimetry give data in agreement with standard reference methods, as typified by the examples in Table 1.

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.

![Graphical response of analyzer](image)

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration as Determined by Standard NIOSH Methods</th>
<th>Analyzer Reading (ppb)</th>
</tr>
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<tbody>
<tr>
<td>NO2</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>104</td>
</tr>
<tr>
<td>NO plus</td>
<td>200</td>
<td>202</td>
</tr>
<tr>
<td>NO2</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

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.

**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 Colorimetry Detector offers a new solution to lab or on-line monitoring. This detector is low in maintenance and easy to work with.

- There is no Ethylene interference
- unmatched accuracy at ppb levels
- simple to use by non-technical staff:
  - no GC separations and no complicated set ups
  - 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.