PAC | Application Note

Analysis of Nitric Oxide (NO) in Ethylene by Gas Chromatography and Chemiluminescence using AC SeNse detector.

SeNse

- Ultra low detection limits
- Excellent Sensitivity, Repeatability & Linearity
- Robust Solution using AC SeNse detector

Keywords: SeNse, Nitric Oxide (NO), Ethylene

INTRODUCTION

This application note describes the determination of trace levels of Nitric Oxide (NO) content in high purity grade Ethylene, using the novel PAC SeNse detector. The SeNse Nitrogen Chemiluminescence detector is highly sensitive to nitrogen, linear, equimolar, and selective; in this particular application no interference or quenching from co-eluting hydrocarbons is observed. Nitric oxide in ethylene should be strictly monitored for production and storage of the bulk product. Due to the inherent property of the NO molecule, a radical, it can pose a safety hazard during storage; it induces spontaneous radical initiated polymerization. Besides the safety issues, it interferes with the catalytic polymerization of ethylene resulting in branched polymers in stead of the long linear chains for High Density PolyEthylene (HDPE).

INSTRUMENTAL

The sample is introduced on the analytical column by switching the sample loop in the carrier gas stream. The capillary PLOT column separates the trace NO from the matrix in an isothermal run. The capillary column is coupled to a high temperature furnace where the nitrogen containing compounds are combusted under oxidative conditions. After oxidation, the nitrogen oxides pass a secondary high temperature zone where thermal degradation of to NO takes place. The furnace effluent is transferred to a reaction cell. Ozone is added to the reaction cell where it reacts with the NO to create exited state nitrogen dioxide. Relaxation of nitrogen dioxide to the ground state releases a photon. The emitted light is measured using a photomultiplier tube and converted to a voltage.

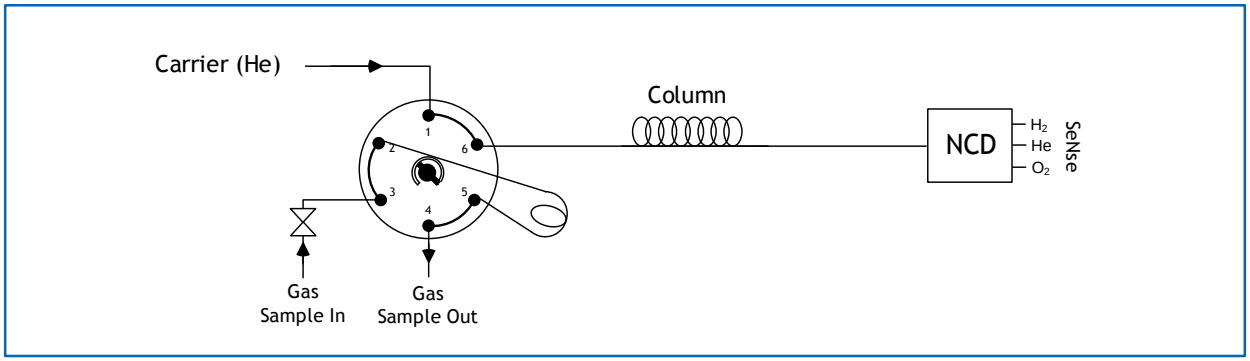

Figure 1: Plumbing diagram for NO in Ethylene using PAC SeNse detector.

VALIDATION

The system and methodology of the AC Nitric Oxide in Ethylene application using PAC SeNse detector is thoroughly tested for separation efficiency, repeatability, detection levels, response linearity and recovery.

REPEATABILITY

Area (concentration) and retention time are the two primary measurements in gas chromatography. The precision in which they are measured ultimately determines the validity of the generated quantitative data. Retention time and area precision require that all parameters (temperatures, pressure, flow, injection) are controlled to exact tolerances. Furthermore, the inertness of the flow path can considerably affect area precision, especially for active nitrogen components at low levels.

Run #	Area (+/- 100 ppb)
	Nitric Oxide
1	27.62
2	28.47
3	30.95
4	30.18
5	30.02
6	30.84
7	30.03
8	31.82
9	29.05
10	30.73
Average	29.97
RSD	4.2%
stdev measured (Concentration)	1.3

Table 1: Area repeatability of a diluted standard blend by GSV introduction

CONCENTRATION REPEATABILITY

Concentration repeatability is measured for 10 consecutive runs for a calibration standard blend diluted with pure Ethylene to ~ 100 ppb single peak. Very good repeatability values are obtained (Table 1 & Figure 2).

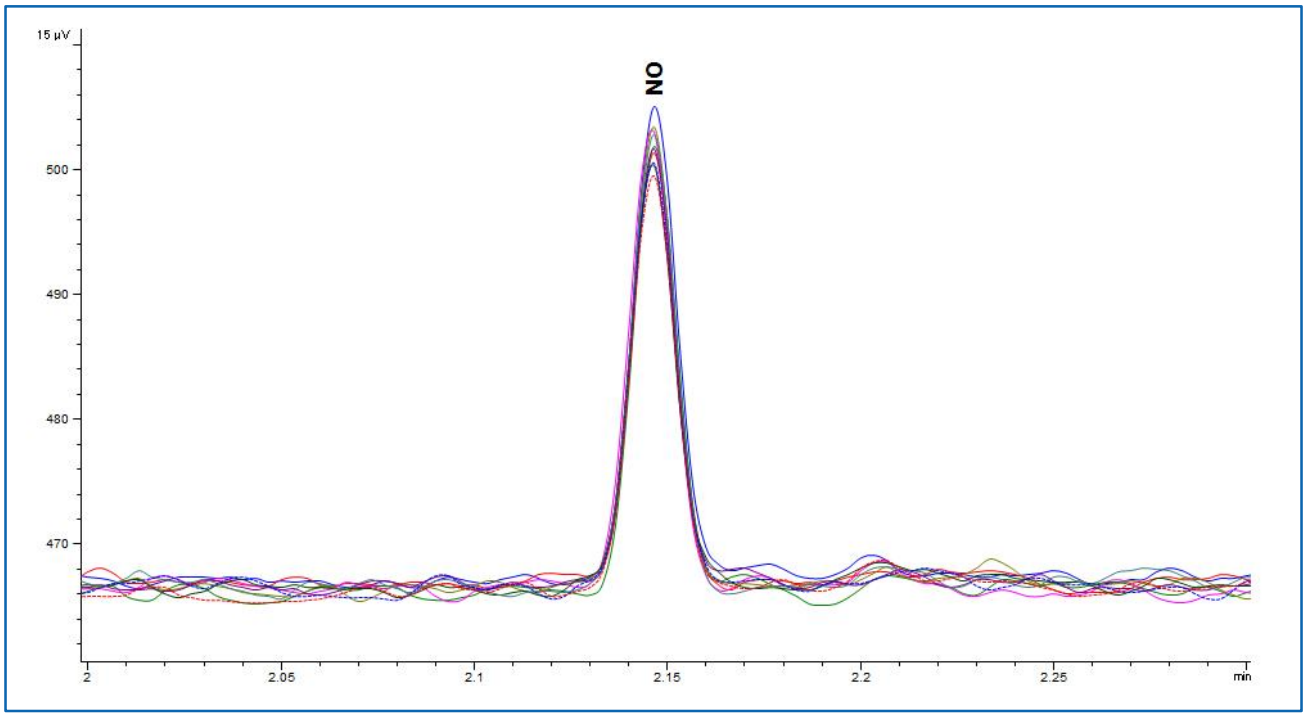

Figure 2: Repeatability overlay of 10 consecutive runs of calibration gas diluted to ~ 100 ppb.

LINEARITY

The linearity of response for the analyzer is verified by creating dynamic dilutions of a certified calibration gas. The dilutions are prepared by combining the calibration gas (Nitric Oxide in Nitrogen) and dilution gas (pure Ethylene) using two separate mass flow controllers. Concentrations from ~ 3000 ppb down to 30 ppb have been created and analyzed on the AC SeNse system. A Calibration line has been prepared for NO and has a linearity correlation > 0.9999.
(Figure 3 & 5)

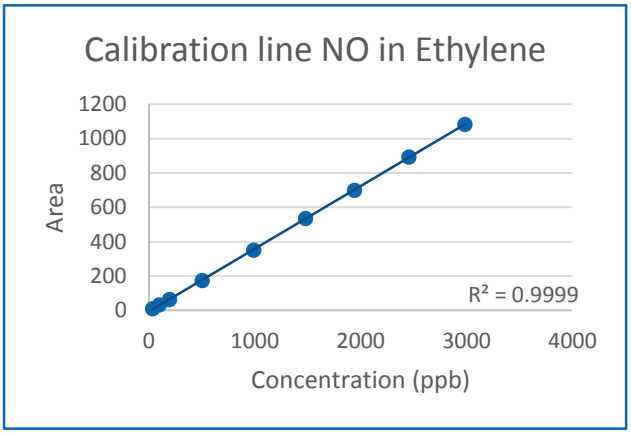

Figure 3: Linearity Plot NO

SEPARATION EFFICIENCY

The SeNse NCD shows an outstanding performance in selectivity towards Nitrogen. Figure 4 shows an overlay chromatogram of the calibration standard: 100 ppb in Ethylene. The blue plot shows zero hydrocarbon breakthrough on the NCD at the retention time of the bulk Ethylene matrix. The red plot shows the FID signal which has been recorded in order to show chromatographic separation of NO and bulk matrix. The small peak in front of the Ethylene bulk peak is Ethane, which is always present in Ethylene.

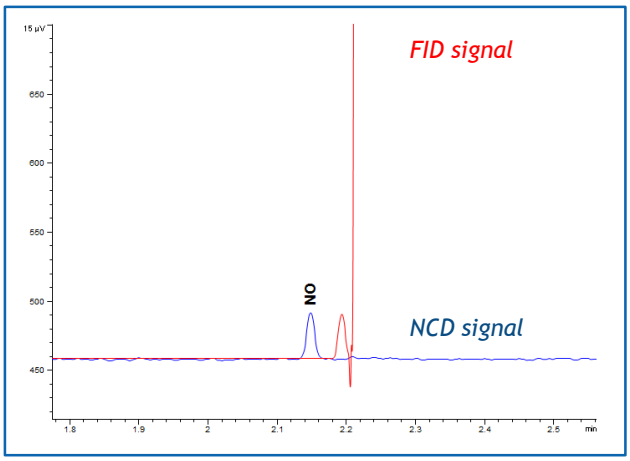

Figure 4: Column efficiency

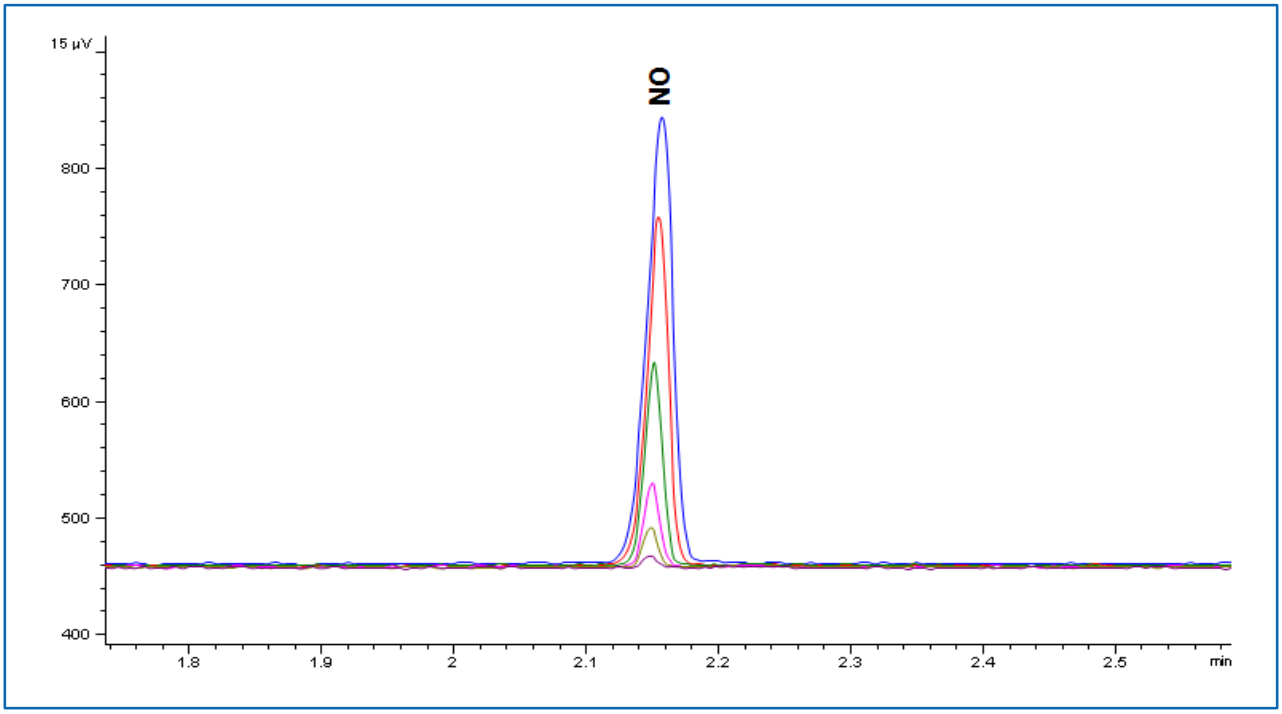

Figure 5: Overlay diluted Calibration gas. 30 ppb (purple) to 3000 ppb (Blue).

DETECTABILITY

Detection limit is calculated according the next formula. The calculations are based on a ~ 100 ppb diluted calibration gas. Results are listed in Table 2.

$$LDL = \frac{3 * c * N}{A} * W * 60$$

Where:

LDL = Limit of detection (ppb mol)

c = Concentration of component of interest (ppb mol)

N = Noise (peak to peak) (µV)

A = Area of peak of interest (µV * s)

W = Width of peak at half height (minutes)

To verify the calculated detectability of the AC NO in Ethylene system, the calibration gas is diluted (as described above under "linearity") down to 30 ppb level and analyzed on the system.

Component	Noise (µV)	Area (µV*s)	Conc. (ppb)	Width (min)	LDL (ppb)
Nitric Oxide	1.5	30.0	100	0.015	< 30

Table 2: Detection limit calculation

CONCLUSION

The AC NO in Ethylene analyzer is a dedicated solution for accurate and repeatable determination of Nitric Oxide using the AC SeNse Nitrogen Chemiluminescence Detector. The application shows a detection limit better than 30 ppb and an excellent linearity and stability in the desirable measuring range. The well known easy operation and robustness of the AC SeNse detector makes this application perfect for continues control of your Ethylene production stream.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer® , DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.