# Analysis of Trace 2-Ethylhexyl Nitrate in Diesel Using Chemiluminescence Detector (NCD)

## Application Brief

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HPI

An increase in the use of fleet diesel vehicles has helped define requirements for diesel fuel for light duty engines. One of these requirements is to recognize the influence of the cetane number on cold start properties, exhaust emissions and combustion noise. Several types of chemicals such as alkyl nitrates, ether nitrates or nitroso compounds have been identified as effective in increasing the cetane number. The most commonly used cetane enhancer is 2-ethylhexyl nitrate (2-EHN). ASTM D4046 standard test method is used for determining the amount of alkyl nitrate added to diesel fuel to judge compliance with specifications covering any alkyl nitrate. This method uses spectrophotometry with a detection range of 0.03 to 0.30 volume percent. The Agilent 7890A GC system configured with a chemiluminescence detector (NCD) provides an alternative method to ASTM D4046 with excellent results. Although the detection of 2-EHN is very difficult because of its low concentration in diesel fuel, a NCD can deliver both the required sensitivity and selectivity as shown in this analysis report.

## Experiment

*Table 1. Typical GC Conditions*

| | |
|---|---|
| Inlet: | 250 °C, Split: 10:1 |
| Column: | HP-5MS, 15 m × 0.32 mm, 0.32 µm, 3.9 mL/min, constant flow: |
| Oven: | 60 °C (2 min), to 280 °C (8 min) at 20 °C/min |
| **NCD** | |
| Temperature: | 200 °C |
| Detector pressure (Torr): | 7.7 |
| Dual plasma controller pressure (Torr): | 110 |
| Burner temperature: | 905 (°C) |
| Hydrogen flow rate (sccm): | 5 |
| Oxidant flow rate (sccm): | 10 (oxygen) |

## Highlights

- High sensitivity in analyzing nitrogen at low ppm levels. The results demonstrate a good signal-to-noise ratio for 2-EHN as nitrogen in diesel at the 1.87 ppm level.
- High selectivity for nitrogen over carbon. Analyzes nitrogen in diesel without suffering from any hydrocarbon interference.
- Linear response simplifies calibration. The results illustrate a linear response to nitrogen (2-EHN) over the concentration range of interest.
- An equimolar response simplifies quantification of unknowns, eliminating the need for determining separate response factors for individual nitrogen compounds.

## Results

The Agilent 255 NCD delivers the sensitivity required for analysis of 2-EHN in diesel without hydrocarbon interference.

Figure 1 shows a good signal-to-noise for 2-EHN as nitrogen in diesel at 1.87 ppm. The result also demonstrates the selectivity of the detector showing no response from the diesel hydrocarbon background.

Trace 2-EHN added to diesel fuel can be found in pump diesel and B20 biodiesel. Figures 2 and 3 show chromatograms with nitrogen species in pump diesel and B20 biodiesel, respectively. The concentration determined for 2-EHN as nitrogen is 1.18 ppm and 18.7 ppm respectively. Also, other higher boiling nitrogen species are observed in both pump diesel and B20 biodiesel.

Figure 3 illustrates linear response to nitrogen (2-EHN) over the concentration range of the interest.

The precision for analysis of 2-EHN in pump diesel with an RSD of 1.15% is shown in Table 2.

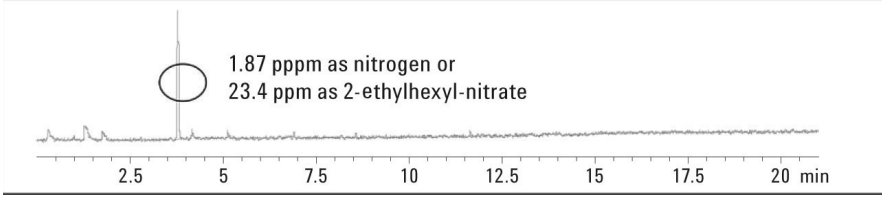


*Figure1. Standard sample: 2-EHN at a concentration of 23.4 ppm in diesel (nitrogen free).*

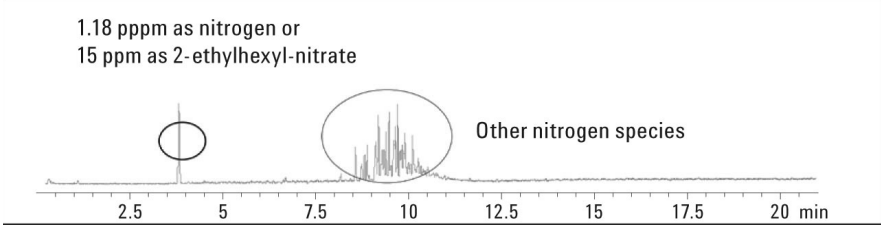


*Figure 2. Nitrogen species in pump diesel fuel.*

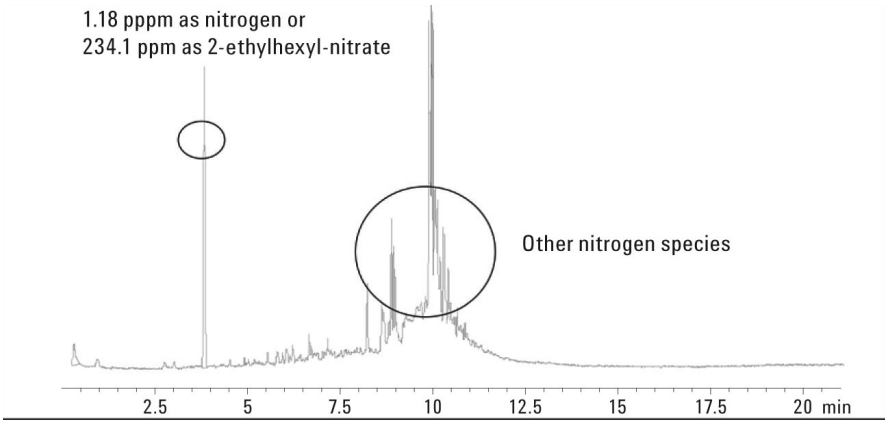


*Figure 3. Nitrogen species in B20 biodiesel.*

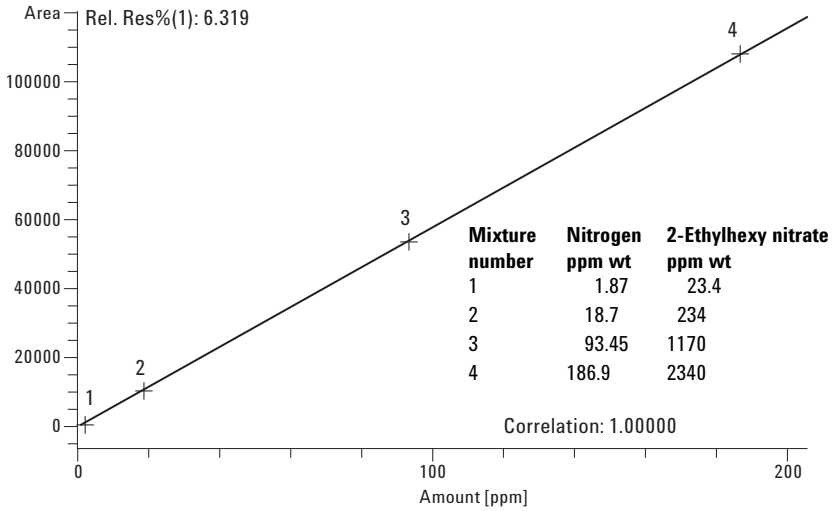


*Figure 4. 2-ethylhexyl nitrate calibration.*

*Table 2. Method precision for analysis of 2-ethylhexyl nitrate in pump diesel.*

| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 | Average | RSD% |
|---|---|---|---|---|---|---|---|---|
| Nitrogen, mg/kg | 1.18 | 1.21 | 1.19 | 1.17 | 1.19 | 1.18 | 1.19 | 1.15 |

Sample run 6 times

## References

1. ASTM D 4046-91(2005), "Standard Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry", Annual Book of Standards, Volume 05.04, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA.
2. Agilent Technical Overview, "Analysis of Trance Nitrogen Species in Benzene," Agilent Technologies publication. 5989-6774EN.

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