Trace Analysis of Ammonia in Ethylene by Gas Chromatography and Nitrogen Chemiluminescence Detection

Application Note

Energy & Chemicals, Polymers

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Abstract

A gas chromatography method was developed for the measurement of trace ammonia in ethylene by capillary gas chromatography (GC) and nitrogen chemiluminescence detection. This method determined the concentrations of ammonia in the parts per billion volume (ppbv) to parts per million volume (ppmv) range. Due to the reactivity problems associated with ammonia, the discussion focuses on low-level linearity and precision.

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Introduction

The measurement of trace ammonia in ethylene is important in the production of polymers and other petroleum-based chemical products. To reach the sub-parts per million volume (ppmv) detection limits required for this industry, the use of a nitrogen chemiluminescence detector (NCD) is required. In the past, NCDs have experienced coking on the internal catalyst tube due to high-concentration hydrocarbon matrices. Over time, this caused a decrease in detector response. As a result, complex valve configurations were necessary to either vent the hydrocarbon matrix so it did not reach the detector, or increase the oxidizer gas to the detector to decoke the catalyst tube. The Agilent 8255 NCD uses electronic pressure control (EPC), giving it the ability to automatically adjust the oxidizer flow rate, and decoke without the use of a complex valve system. This Application Note discusses a fast and simple GC configuration to analyze ammonia gas to low parts per billion volume (ppbv) levels in light hydrocarbons.

Experimental

The instrument consists of an Agilent 7890B GC configured with an Agilent 8255 NCD, and a 6-port gas sample valve. The gas sample valve uses a 1-mL gas sample loop, directly injected on a megabore column, (p/n CP8590, Select Low Ammonia). All sample-wetted surfaces were stainless steel deactivated with an Agilent UltiMetal Plus treatment. Instrument control, data acquisition, and data analysis were performed using the Agilent OpenLAB CDS data system.

The ammonia analysis procedure began by purging the sample loop with standard or sample. After the sample introduction purge, the 6-port gas sample valve (Valve 1) was switched on to inject sample. After 0.25 minutes, Valve 1 was switched off. During the analysis, the oxidizer flow was set to remain at the maximum flow of 30 mL/min. The high oxidizer flow prevents catalyst coking when the matrix hydrocarbons pass through the detector. Just before ammonia eluted to the detector, the oxidizer flow was automatically set to 4 mL/min. This allowed the ammonia to be analyzed under optimum flow conditions. After ammonia elution, the high 30 mL/min oxidized flow was re-established to prevent further coke formation. Figure 1 shows an example chromatogram.

Chromatographic conditions

Temperatures	
Valve/valve box	125 °C
Column oven	100 °C (hold 0.25 minutes), ramp 25 °C/min to 150 °C (hold 2.75 minutes)
NCD Base	200 °C
NCD Burner	900 °C
Flows	
Column 1	10 mL/min
NCD Oxidizer flow	30 mL/min
NCD Hydrogen flow	Off
Valve timing	
Valve 1 (6-port)	On at 0.01 minutes, off at 0.25 minutes

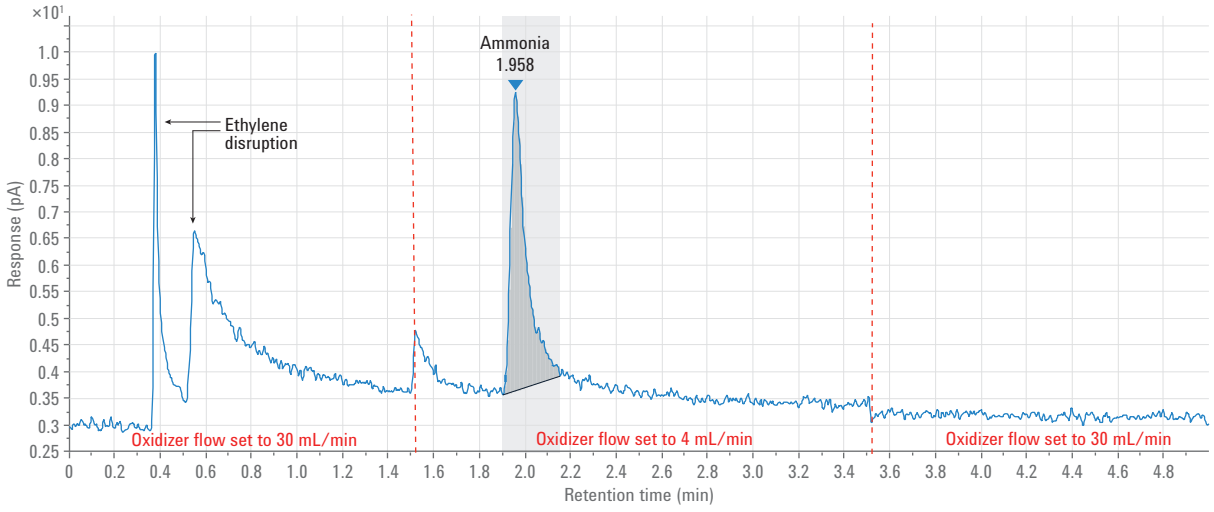
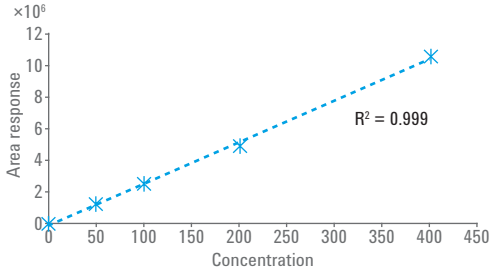


Figure 1. Example chromatogram, 50 ppbv ammonia.

Results and Discussion

Linearity

To establish an R^2 value, trace level ammonia linearity was investigated by analyzing four different concentrations, with the addition of the origin. Figure 2 shows the results. The analysis resulted in an R^2 value of 0.999 from 50 to 400 ppbv, including the origin. A 500 ppbv ammonia in ethylene gas standard with a dynamic dilution system was used to generate the various concentration levels.

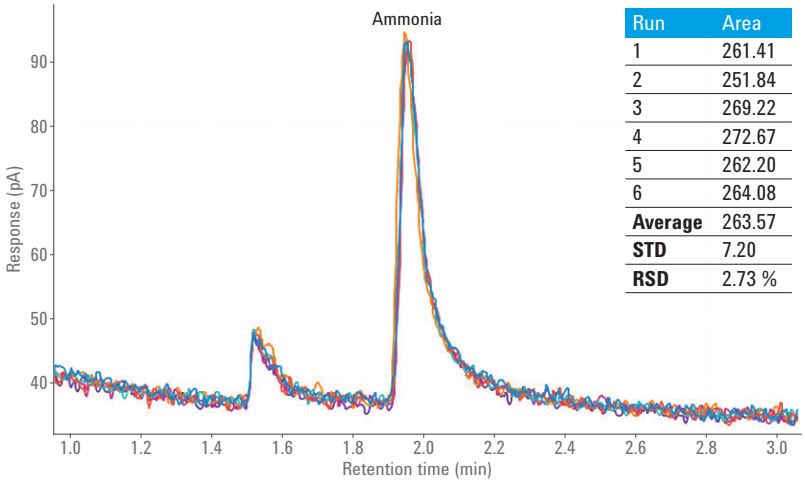


Concentration (ppbv)	Area
0	0
50	1,279,093
100	2,547,019
200	4,927,718
400	10,597,983

Figure 2. Ammonia linearity.

Precision

Precision was investigated by analyzing six consecutive replicates of a 50 ppbv standard to establish relative standard deviation (RSD). RSD was reported at 2.73 %. Figure 3 shows the results.



Run	Area
1	261.41
2	251.84
3	269.22
4	272.67
5	262.20
6	264.08
Average	263.57
STD	7.20
RSD	2.73 %

Figure 3. Precision: ammonia 50 ppbv.

Conclusion

The Agilent 7890B GC configured with the Agilent 8255 NCD provides a simple and fast way to analyze trace ammonia in light hydrocarbons. Automated changes to the NCD oxidizer flow optimize ammonia response and reduce adverse matrix effects in the detector. Over time, this technique maintains system uptime by reducing maintenance. The approach provides the sensitivity, reproducibility, and linearity required for the hydrocarbon industry. Note that performance improvements can be obtained using all UltiMetal Plus sample tubing including regulators and fittings.

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Published in the USA, May 5, 2017
5991-8061EN

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