

Catalytic Ammonia Cracking: Reaction Monitoring Using the Agilent 990 Micro GC System

Monitoring from zero to greater than
99.9% conversion

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Abstract

Ammonia (NH_3) decomposition facilitates hydrogen production. Monitoring the reactants and contaminants of ammonia decomposition, including NH_3 , H_2 , N_2 , and H_2O , is highly important for catalytic performance as well as activity measurements. In this work, an Agilent 990 Micro GC system configured with an Agilent CP-Molsieve channel and an Agilent CP-Volamine channel is demonstrated to analyze NH_3 , H_2 , N_2 , and H_2O across a wide concentration range. Notably, the analysis can be completed within one minute. The method's performance, including repeatability, linearity, limit of detection (LOD) and carryover was evaluated, and the results were satisfactory.

Introduction

NH₃ has tremendous potential as a clean liquid fuel. NH₃ may play an essential role in the decarbonization of hard-to-abate sectors, such as shipping, power generation, and heavy-duty transportation, which will accelerate the global journey to net zero and facilitate sustainable development.¹ Composed entirely of hydrogen and nitrogen, NH₃ itself can be employed as an energy source with the potential for zero "tailpipe" carbon emissions. NH₃ can also be catalytically decomposed to its constituent elements as a convenient way to transport and store clean hydrogen.²

The ammonia decomposition reaction (2NH₃ → N₂ + 3H₂) facilitates hydrogen (H₂) and nitrogen (N₂) production. Each mole of NH₃ generates two moles of gas (0.5 mol N₂, 1.5 mol H₂), creating a self-dilution effect. As a result, a reactor at 50% conversion with an ultrahigh purity NH₃ feed will create an effluent stream containing only 33% NH₃. Therefore, the conversion must be calculated using Equation 1.

Equation 1.

$$X = \frac{1 - \frac{y_{\text{NH}_3, \text{out}}}{y_{\text{NH}_3, \text{in}}}}{1 + y_{\text{NH}_3, \text{out}}}$$

Where $y_{\text{NH}_3, \text{in}}$ is the mol fraction of ammonia entering the reactor, and $y_{\text{NH}_3, \text{out}}$ is the mol fraction of ammonia exiting the reactor (that is, into the GC).

Failure to calculate conversion using Equation 1 may lead to erroneous measurements of catalytic performance and can inflate the perceived activity (for example, 50 versus 67% conversion).

With the constant improvement of emission-free, high-energy-density, ammonia-based power solutions, there is a pressing need for monitoring reactants and contaminants. Monitoring devices should be capable of measuring the

required components (NH₃, H₂, N₂, and H₂O) over a wide concentration range. Furthermore, these devices should have a short response time, be inert towards reactants, and, if possible, be able to monitor multiple reactor systems or lines.

For this work, a 990 Micro GC system was used to measure NH₃, H₂, N₂, and H₂O simultaneously. While the analysis of N₂ and H₂ using a Molsieve column in gas chromatography is well established, the methods for analyzing water and ammonia are less developed.

In previous studies, the basic analysis of NH₃ (up to concentrations of 20%) was demonstrated using a CP-Volamine channel. In a six-month robustness test, the 990 Micro GC system and the CP-Volamine analytical channel both proved to be effective and durable over an extended period of time.³ The J&W CP-Volamine column used in the channel is a relatively nonpolar column that is highly effective for the analysis of NH₃ or other polar components. A unique deactivation process is applied during manufacturing, which gives higher quality peak shapes for NH₃ compared to other column chemistries or deactivation

processes. Higher quality peak symmetry can lead to lower detection limits, higher precision, and improved accuracy. The goal of this study was to demonstrate that the 990 Micro GC system can effectively analyze 100% NH₃ without compromising performance or robustness.

Experimental

The 990 Micro GC system was equipped with a 10 m Agilent J&W CP-Molsieve 5Å backflush channel and a 15 m CP-Volamine straight channel. Table 1 shows the experimental conditions. The Molsieve channel was used to analyze H₂ and N₂, while the Volamine channel was used to analyze NH₃ and H₂O.

Sample flow to the Micro GC was set to continuous flow, and the inlet port pressure was controlled as shown in Figure 1. Flow-through stream selection valves were used for sample switching between the reactor inlet and outlets, multiple reactors, and calibration gases. The cycle time, including sampling and separation, was approximately one minute, allowing 60 measurement cycles per hour.

Table 1. Test conditions for the NH₃/H₂/N₂/H₂O mixture.

Channel Type	10 m Agilent J&W CP-Molsieve 5Å Column, 1 m Backflush	15 m Agilent CP-Volamine Column
Carrier Gas	Argon	Helium
Column Pressure	29 psi	22 psi
Injector Temperature	110 °C	110 °C
Column Temperature	80 °C	50 °C
Injection Time	40 ms	40 ms
Backflush Time	4.5 s	NA
Invert Signal	On for H ₂ only	Off
Sampling Time	30 s	

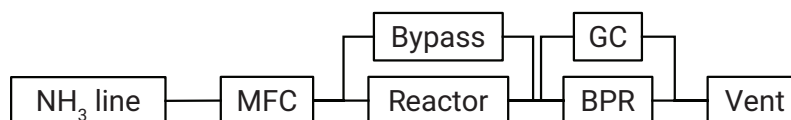


Figure 1. System setup including the Agilent 990 Micro GC inlet port pressure control. MFC denotes mass flow controller, and BPR denotes backpressure regulation.

Tuning the backflush time on the Molsieve channel was based on the nitrogen/hydrogen composite peak elution. It is important to optimize the backflush time to avoid ammonia eluting onto the Molsieve column, which can lead to shifting retention times (RTs). NH₃ behaves like H₂O and CO₂ on a Molsieve column, where it strongly adsorbs and occupies cavities inside the molecular sieve structure, decreasing the retention of the column. A bakeout of the Molsieve column can regenerate its performance.

This system is best set up in a well-ventilated area (fume hood). Although the 990 Micro GC system allows piping exhaust streams into a vent line rather than exhausting into the laboratory space, analysis of high concentration NH₃ requires ventilation for safety reasons.

As shown in Table 2, calibration gases were prepared using calibrated mass flow controllers (Alicat MC-series) to control flow rates of pure NH₃ (0 to 100%), H₂ (0 to 75%), and N₂ (0 to 25%). For NH₃ calibration, it was observed that at low concentration levels, the NH₃ response factor was lower than the response factor at percent concentration levels. Therefore, a separate calibration curve was developed for NH₃ from 9 to 5,000 ppm. The 5,000 ppm NH₃/N₂ gas was diluted to different calibration levels (Table 2).

For water calibration, a syringe pump was used, allowing injection directly into a heated ¼-inch tee manifold on the gas line, leaving no visible condensation in the system. Calibrated concentrations for water were 0.1 to 1.5%. Additionally, for the determination of the lower limit of detection (LOD), a certified gas mixture of 8.996 ppm NH₃ in N₂ (Airgas) was sampled more than 500 times.

The following test results were produced during the collaboration between Agilent and Amogy.⁴

Table 2. Calibration mixtures with component concentrations at percent levels and calibration mixtures with low concentrations of NH₃ ranging from 9 to 5,000 ppm in N₂.

Calibration Levels	Calibration Mixtures (Percent Levels)			Calibration Mixtures (Low NH ₃ Concentrations in ppm)
	%NH ₃	%H ₂	%N ₂	
1	0	75	25	5,000
2	3	72.75	24.25	2,500
3	5	71.25	23.75	1,250
4	10	67.5	22.5	625
5	15	63.75	21.25	250
6	20	60	20	125
7	40	45	15	50
8	60	30	10	25
9	80	15	5	9
10	100	0	0	

Results and discussion

Separation

Figures 2 and 3 show typical chromatographic separations on Volamine channels. The chromatogram for 8.996 ppm NH₃ used for LOD calculation is shown in Figure 4. The Volamine channel allows baseline

separation of NH₃ and water, with H₂ and N₂ eluting as a composite peak in front. Separation of H₂ and N₂ on the CP-Molsieve column is well documented in various other application notes.^{5,6} Here, H₂ and N₂ separation on the CP-Molsieve channel is shown in Figure 5. The shape for all peaks was excellent, even at high concentrations.

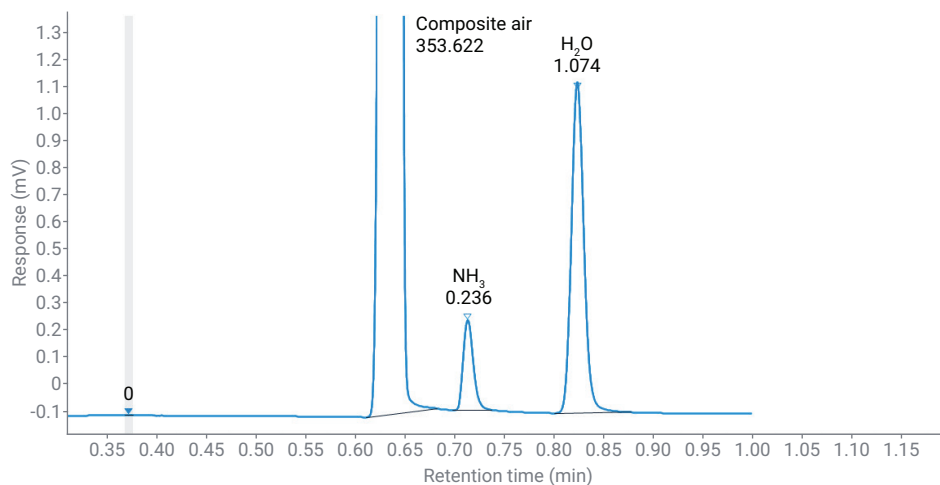


Figure 2. Chromatogram of 300 ppm NH₃ and 1,300 ppm H₂O in H₂:N₂ 75:25% balance on an Agilent CP-Volamine channel. The area responses of target analytes are labeled.

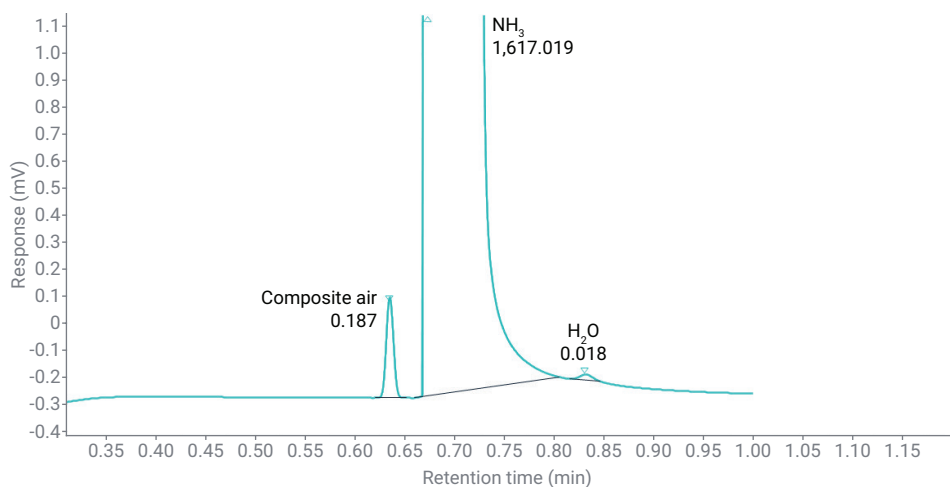


Figure 3. Chromatogram of bulk NH_3 with trace contaminants N_2 and H_2O on the Agilent CP-Volamine channel.

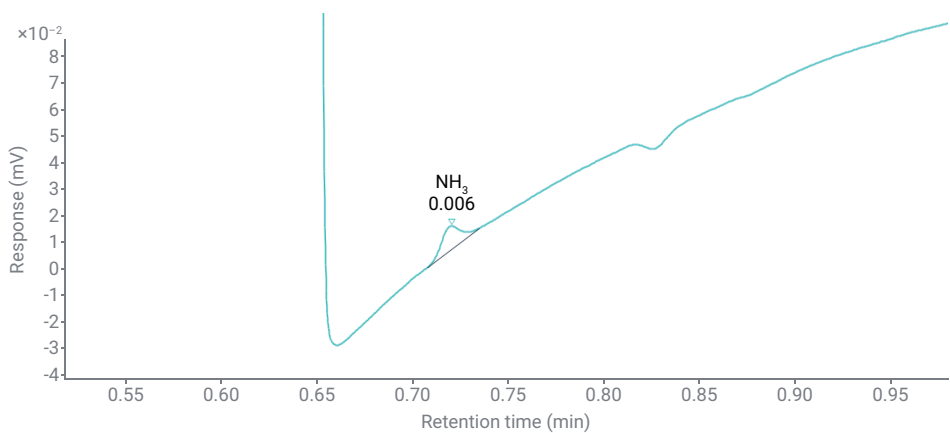


Figure 4. Chromatogram of 8.996 ppm NH_3 on the Agilent CP-Volamine channel.

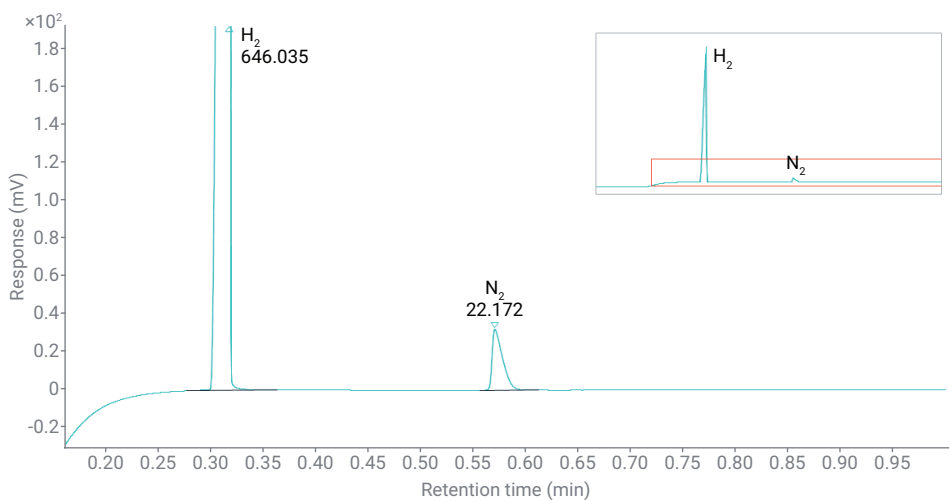


Figure 5. Chromatogram showing H_2/N_2 separation on the Agilent CP-Molsieve channel (mix of 20% NH_3 , 60% H_2 , and 20% N_2).

Calibrations and linearity

Figures 6 to 10 show the calibration curves for NH_3 , N_2 , H_2 , and H_2O , respectively. All curves have a correlation coefficient of 0.999 or better, except for water. The linear fit for water was slightly lower compared to the other components, with correlation > 0.998 . Deviations were attributed to the syringe pump sampling system.

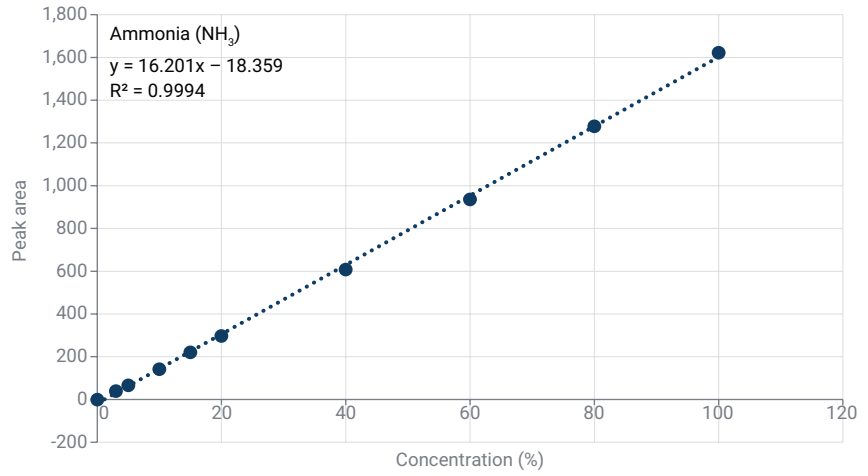


Figure 6. Calibration curve for ammonia (NH_3).

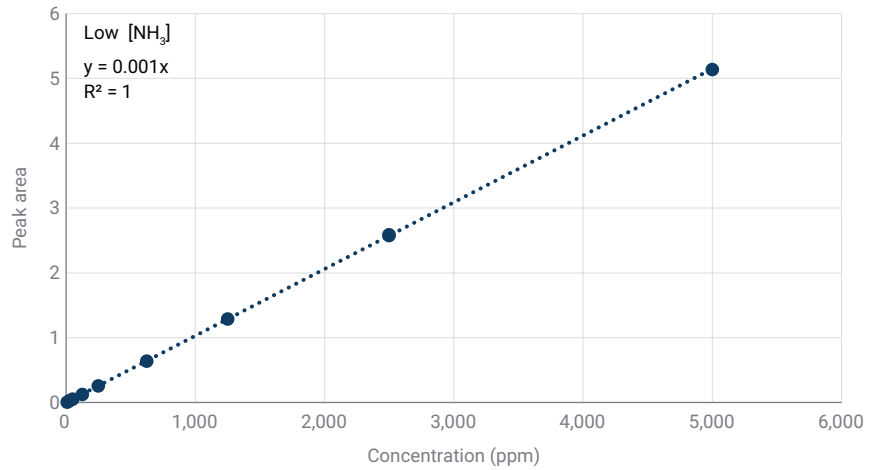


Figure 7. Calibration curve for low concentration ammonia.

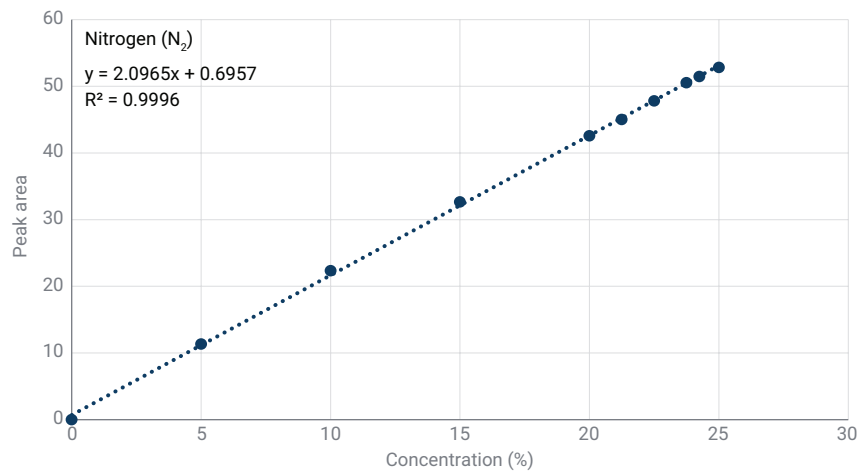


Figure 8. Calibration curve for nitrogen (N_2).

System robustness

To evaluate the robustness of the system, continuous injections of 100% NH₃ were conducted over three weeks, yielding 21,030 total injections. Figure 11 shows peak areas and RTs for NH₃ over the course of this study. The system was shown to be extremely stable for the analysis of ammonia, with a peak area repeatability (% relative standard deviation, %RSD) of only 0.13% and RT repeatability (%RSD) of only 0.07%.

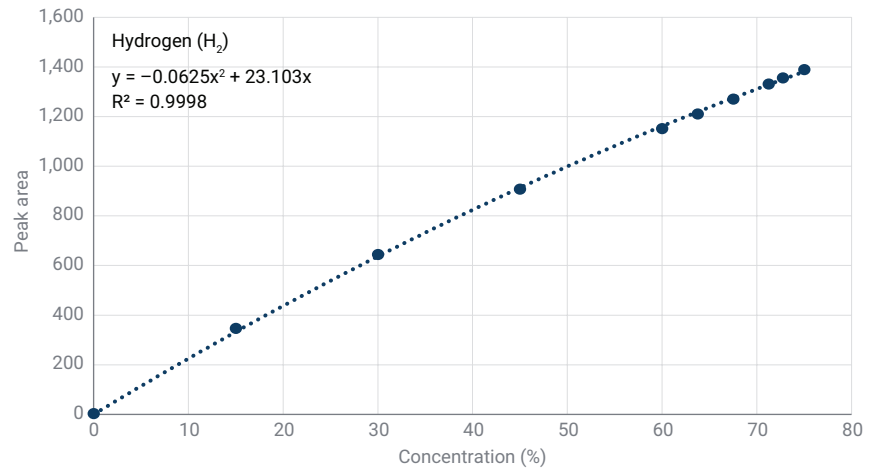


Figure 9. Calibration curve for hydrogen (H₂).

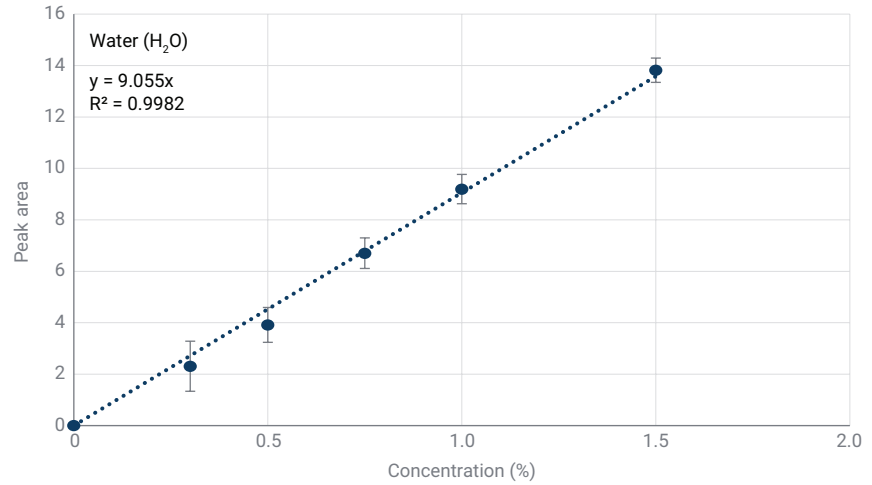


Figure 10. Calibration curve for water (H₂O).

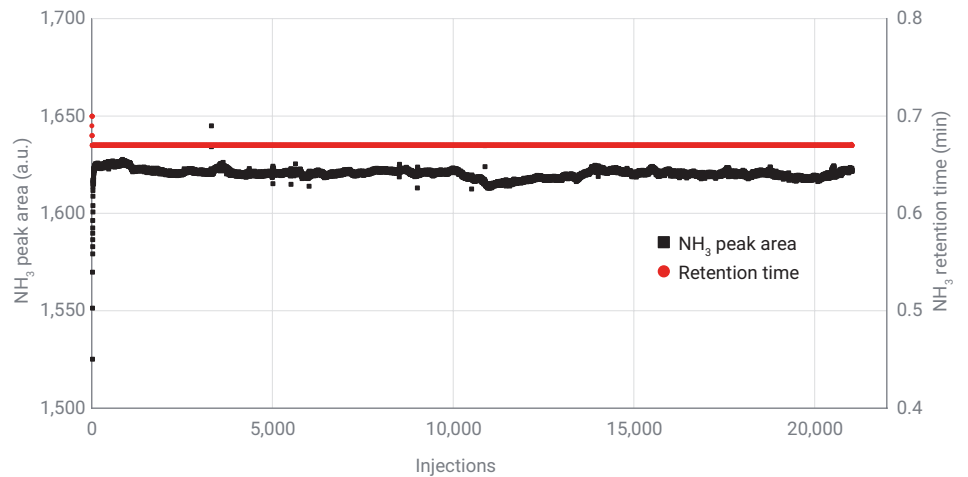


Figure 11. Robustness test for 100% ammonia (NH₃). Approximately 21,000 injections of pure ammonia were conducted over the course of this testing. The black trace shows the NH₃ peak area, while the red trace shows the NH₃ retention time.

Carryover

Some carryover for NH_3 may be expected when switching between bulk ammonia and very low ammonia concentrations. This concentration shift is significant (almost four orders of magnitude), and NH_3 has a high affinity for sticking to metal surfaces. Additionally, a small amount of dead volume in the sample lines requires flushing, despite the use of a sample stream selection valve.

In this experiment, carryover was tested while alternating between sample streams on the reactor every 50 injections. The bulk ammonia sample was 100% NH_3 , while the reformate was approximately 0.03% (300 ppm) NH_3 in a 75:25% $\text{H}_2:\text{N}_2$ mix.

After injecting bulk ammonia for some time, it takes approximately 20 to 30 runs to be within 10% of the actual reformate value (300 ppm NH_3), which is acceptable for this setup. When switching from 300 ppm back to 100% NH_3 , the change to a higher result is almost instantaneous, as expected (not shown in the graph).

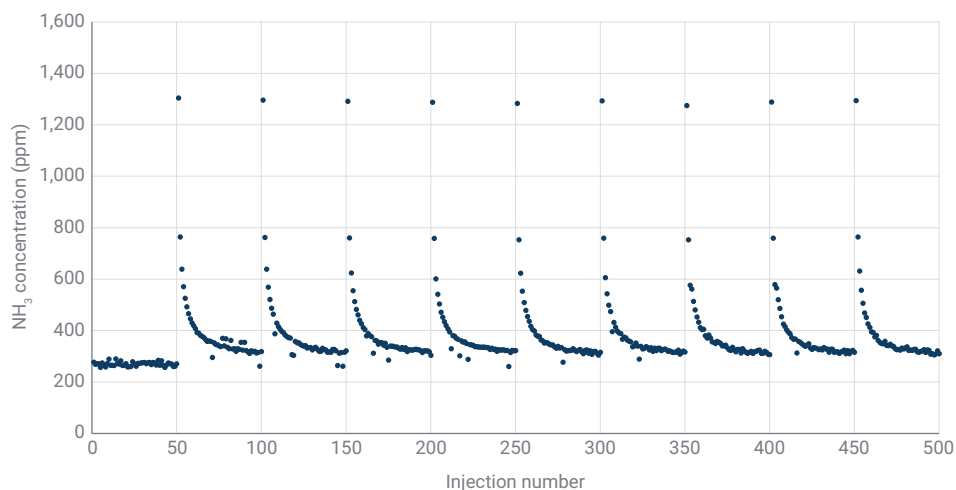


Figure 12. Carryover testing involving the alternation between bulk and reformate samples every 50 injections. Only reformate results are shown.

Precision and estimated detection limit for ammonia

Precision for NH_3 analysis was derived from the robustness test (with 21,030 runs), the carryover experiment, and the analysis of low concentration NH_3 in nitrogen (25 ppm level). Table 3 lists the precision for peak area (repeatability, %RSD) for supply line (bulk), reformate levels (approximately 300 ppm), and low concentration NH_3 standard (25 ppm).

Table 3. Area precision (repeatability, %RSD) for ammonia.

Concentration (NH_3)	Repeatability (%RSD)
Bulk	0.13
298 ppm	2.90
25 ppm	2.58

Based on the results for 50 runs of 8.996 ppm NH_3 , a theoretical LOD for NH_3 can be derived from Equation 2.

Equation 2.

$$\text{LOD} = C_{\text{NH}_3} \times \% \text{RSD} \times t$$

Where:

- t is the single-tailed critical value ($t = 2.679$ for 99% confidence with 50 replicate injections)
- C_{NH_3} is the nominal concentration of NH_3 (8.996 ppm)
- %RSD is the relative standard deviation of the NH_3 response

For 50 runs of 8.996 ppm NH_3 , the area %RSD was 2.71%. Given this, the NH_3 LOD is calculated to be approximately 0.65 ppm.

Conclusion

This application note demonstrates the capabilities of an Agilent 990 Micro GC system for monitoring NH₃, N₂, H₂, and H₂O in the feed and product streams of ammonia cracking reactors. The system has been shown to be effective across a wide range of concentrations.

This two-channel configuration used a 15 m Agilent CP-Volamine straight channel and a 10 m Agilent CP-Molsieve backflush channel, performing exceptionally well for NH₃, N₂, and H₂.

The system was equipped with a stream selection valve (SSV), allowing easy switching between the bulk ammonia source, the low concentration reformat side of the reactor, and the calibration gas flows. The SSV also makes it possible to monitor multiple reactors with a single instrument and is amenable to high-throughput or piloting studies.

This 990 Micro GC setup has demonstrated exceptional repeatability and linearity, a rapid cycle time (< 1 minute), and a robustness towards ammonia as a bulk sample.

References

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