NOx Measurement Errors in Ammonia-Containing Exhaust

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Diesel Engine Emissions Reduction Meeting
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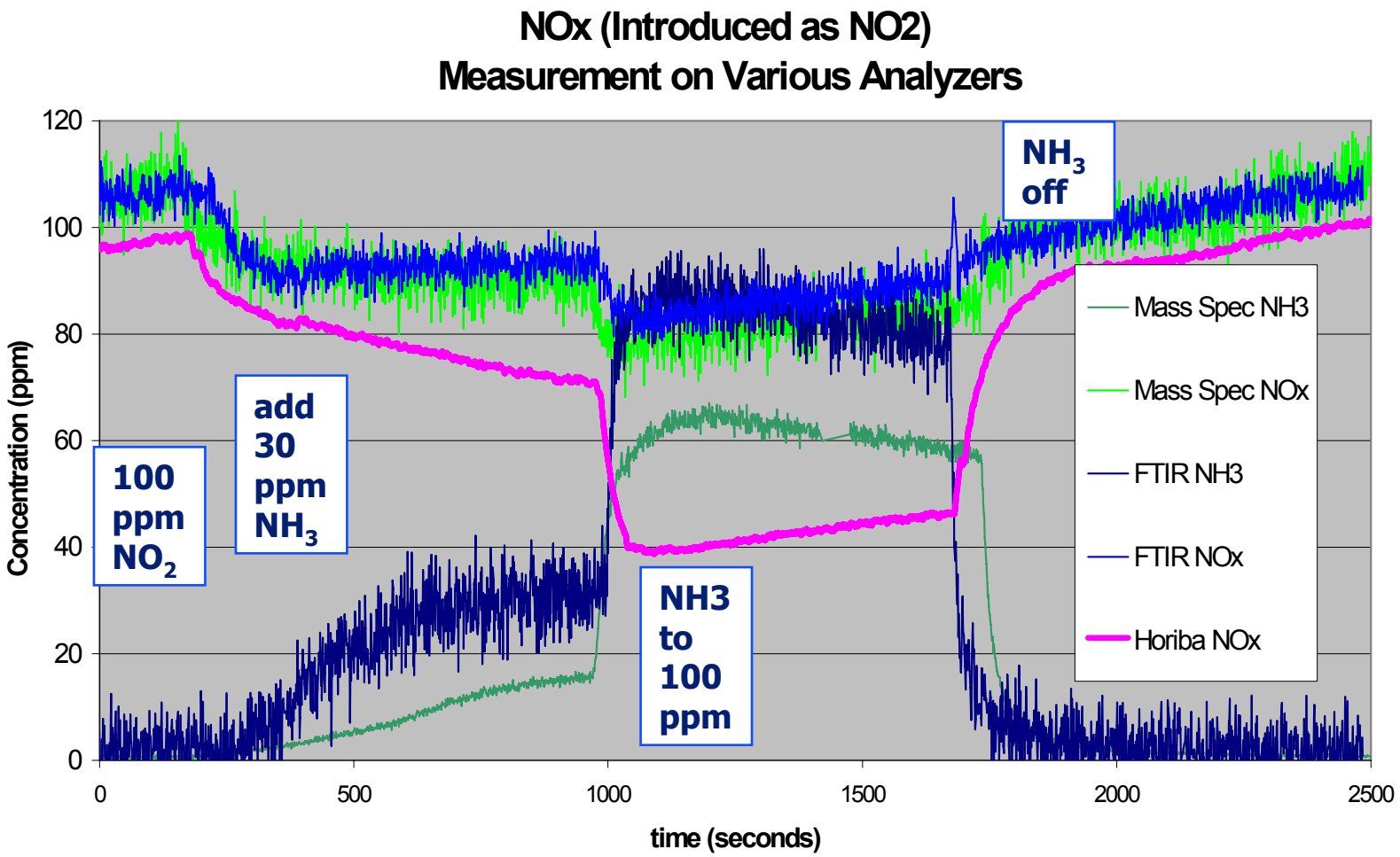
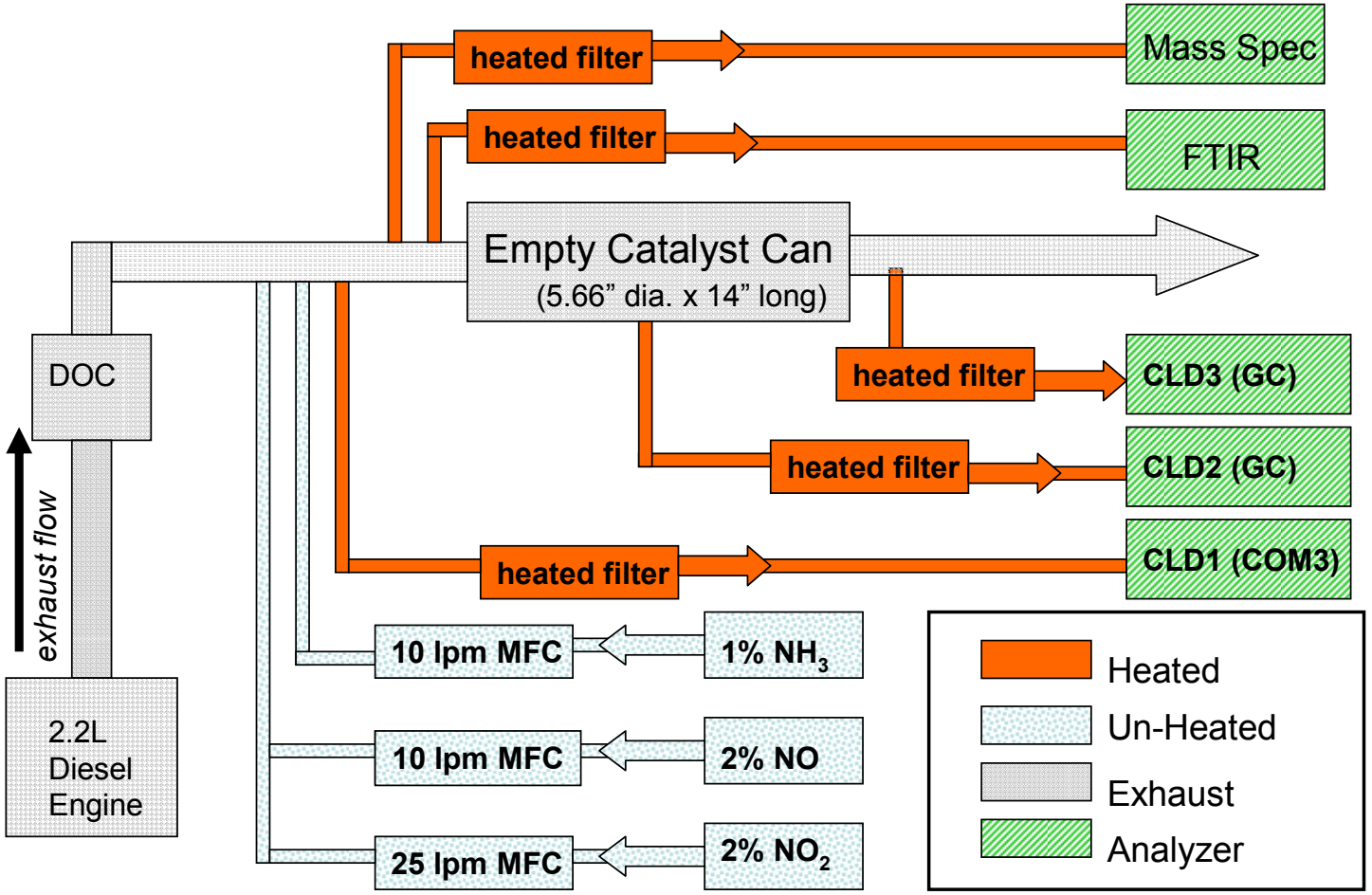
Introduction

- Diesel NOx aftertreatment can lead to ammonia (NH_3) in exhaust
  - Urea-SCR systems
  - LNT systems near end of rich regeneration
  - LNT-SCR combinations
- NH_3 can cause significant measurement errors with various NOx instruments
- Larger issue for engine-out and mid-bed samples

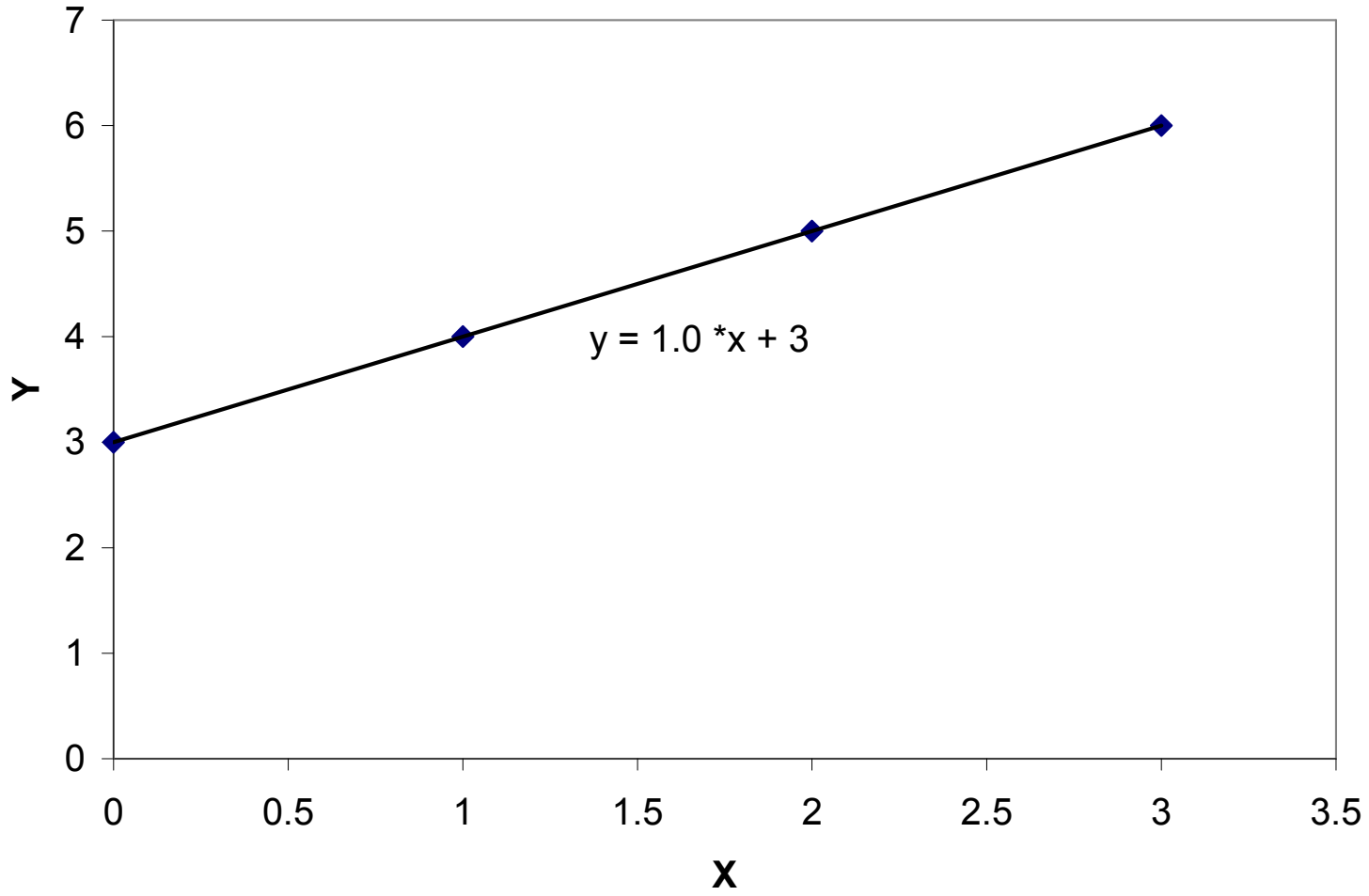
Example of Concern



Experimental Set-up



Standard Addition Test Concept



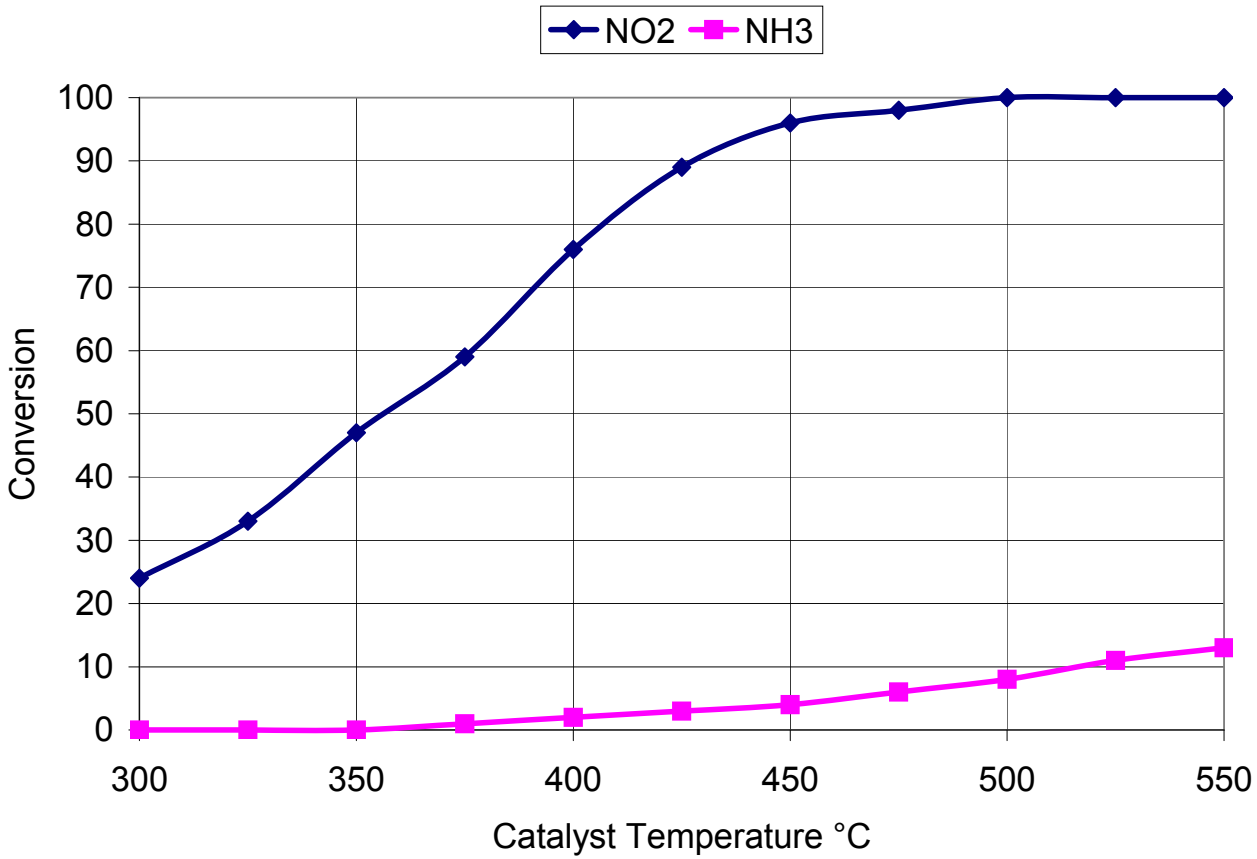
Test Design
Replicate Three

	MFC Settings			Standard Addition to Exhaust				Flow rates			
	NO	NO2	NH3	NO	NO2	NOx	NH3	Total	NO	NO2	NH3
	%	%	%	(ppm)	(ppm)	(ppm)	(ppm)	L/min	L/min	L/min	L/min
1	100	100	0	75	226	301	0	1330	10	15	0
2	100	100	100	75	224	299	149	1340	10	15	10
3	50	100	100	37	225	262	150	1335	5	15	10
4	100	50	100	75	113	188	150	1332	10	7.5	10
5	50	50	100	38	113	151	151	1327	5	7.5	10
6	50	50	50	38	113	151	76	1322	5	7.5	5
7	50	50	0	38	114	152	0	1317	5	7.5	0
8	50	100	0	38	226	264	0	1325	5	15	0
9	50	100	50	38	226	263	75	1330	5	15	5
10	100	50	50	75	113	188	75	1327	10	7.5	5
11	100	50	0	76	113	189	0	1322	10	7.5	0
12	100	100	50	75	225	300	75	1335	10	15	5

Chemiluminescent Analyzer (CLD)

- Developed at Ford Research in early 1970's
- Most common NOx measurement
- Actually measures NO
  - $NO + O_3 \rightarrow NO_2^* + O_2$
  - $NO_2^* \rightarrow NO_2 + photon$
- NO_2 reduced to NO in converter; typical compositions
  - Carbon-molybdenum
  - Molybdenum
  - Carbon
  - Gold
  - Ferrous sulfate
  - Stainless steel

Carbon-Molybdenum Converter

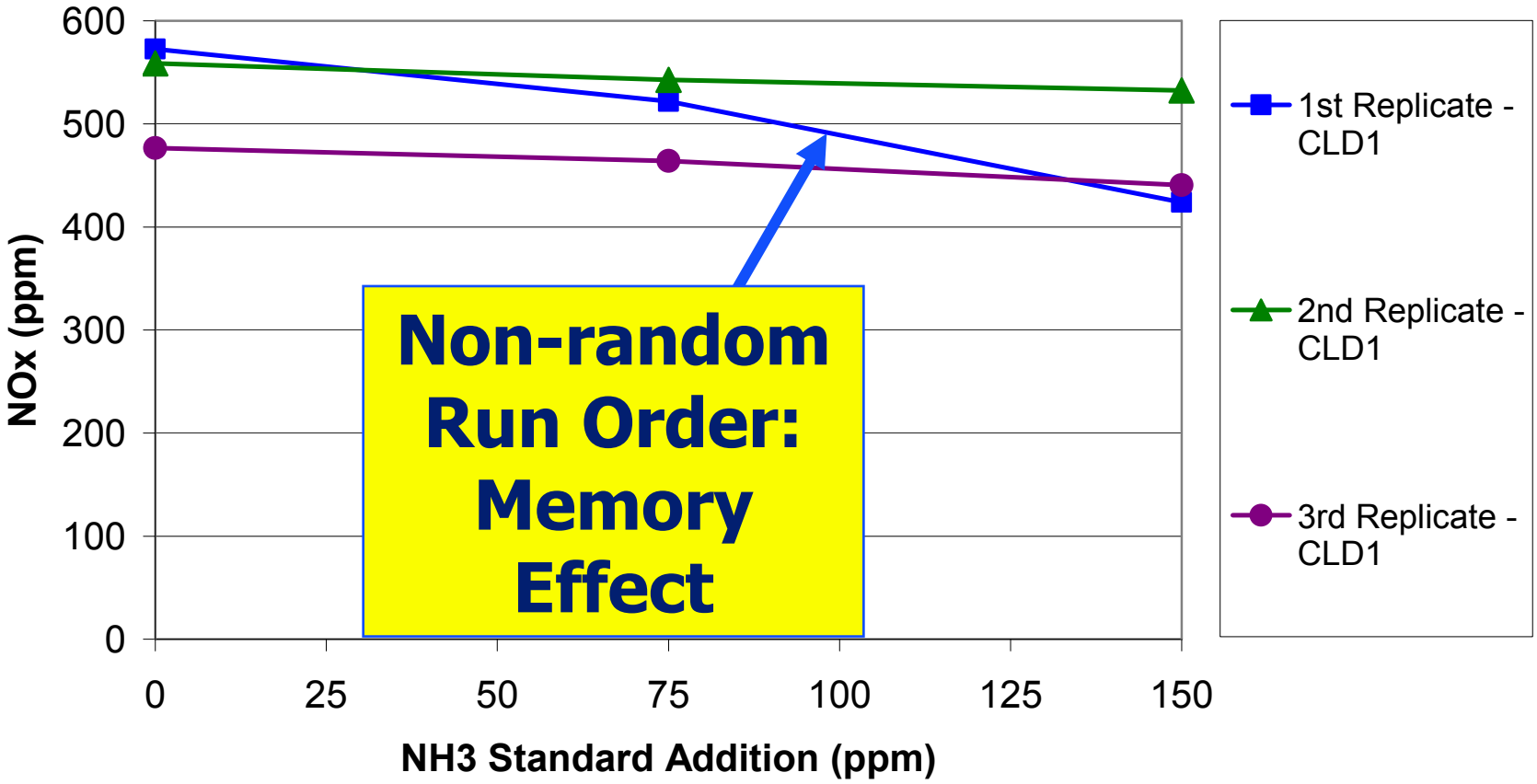


Data from Breitenbach and Shelef

Ammonia Reactions

- NOx can be removed by reactions with ammonia
  - Ammonium nitrate:
    - $3NO_2 + H2O \rightarrow 2HNO_3 + NO$ (1)
    - $NH_3 + HNO_3 \rightarrow NH_4NO_3$ (2)
  - SCR reactions:
    - $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ (3)
- Must keep sample lines above 100°C to avoid ammonium nitrate
- Choose converter that does not promote these reactions

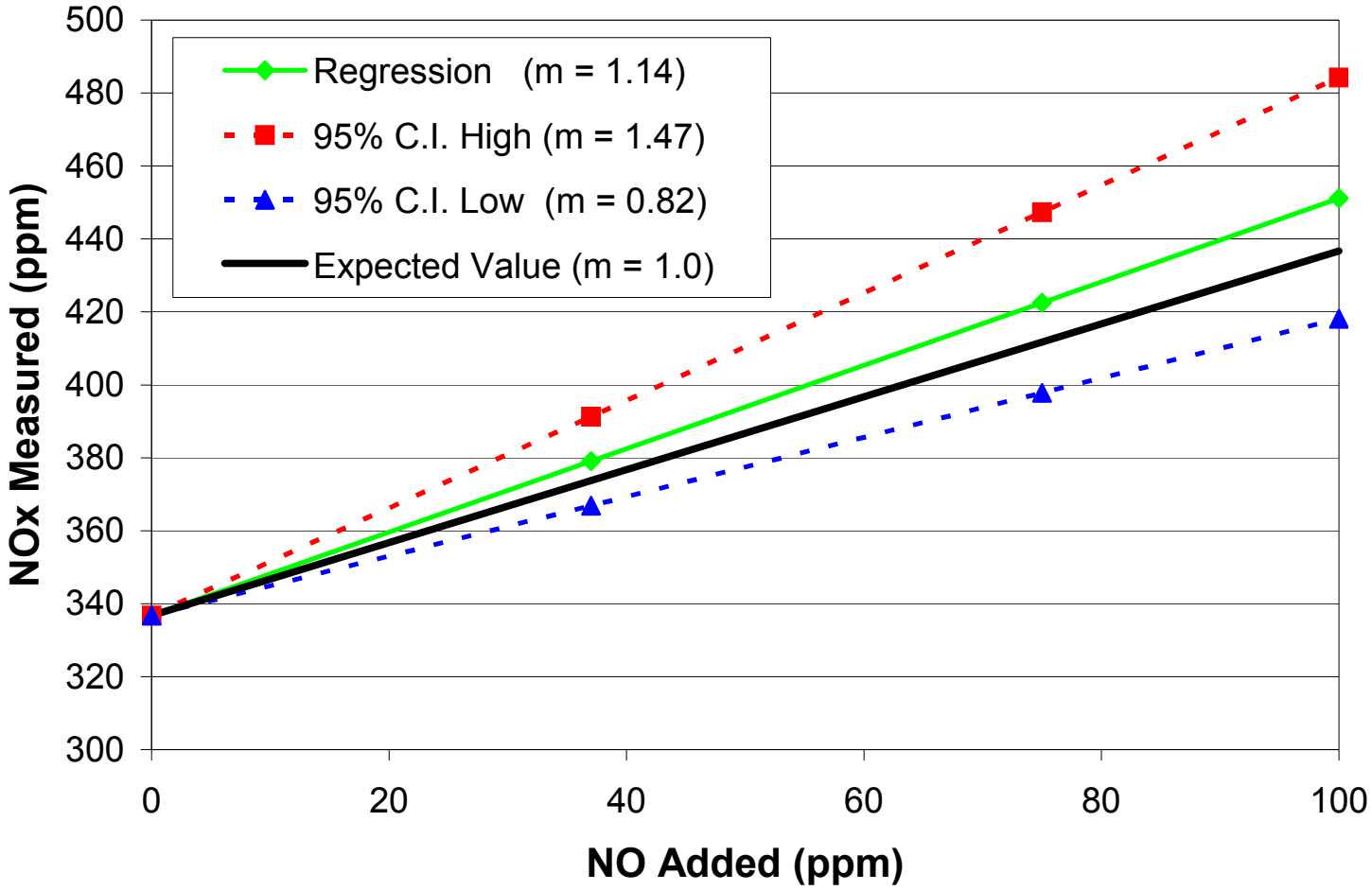
CLD w/ COM3 Converter
Main Effect of NH3 on NOx Measurement



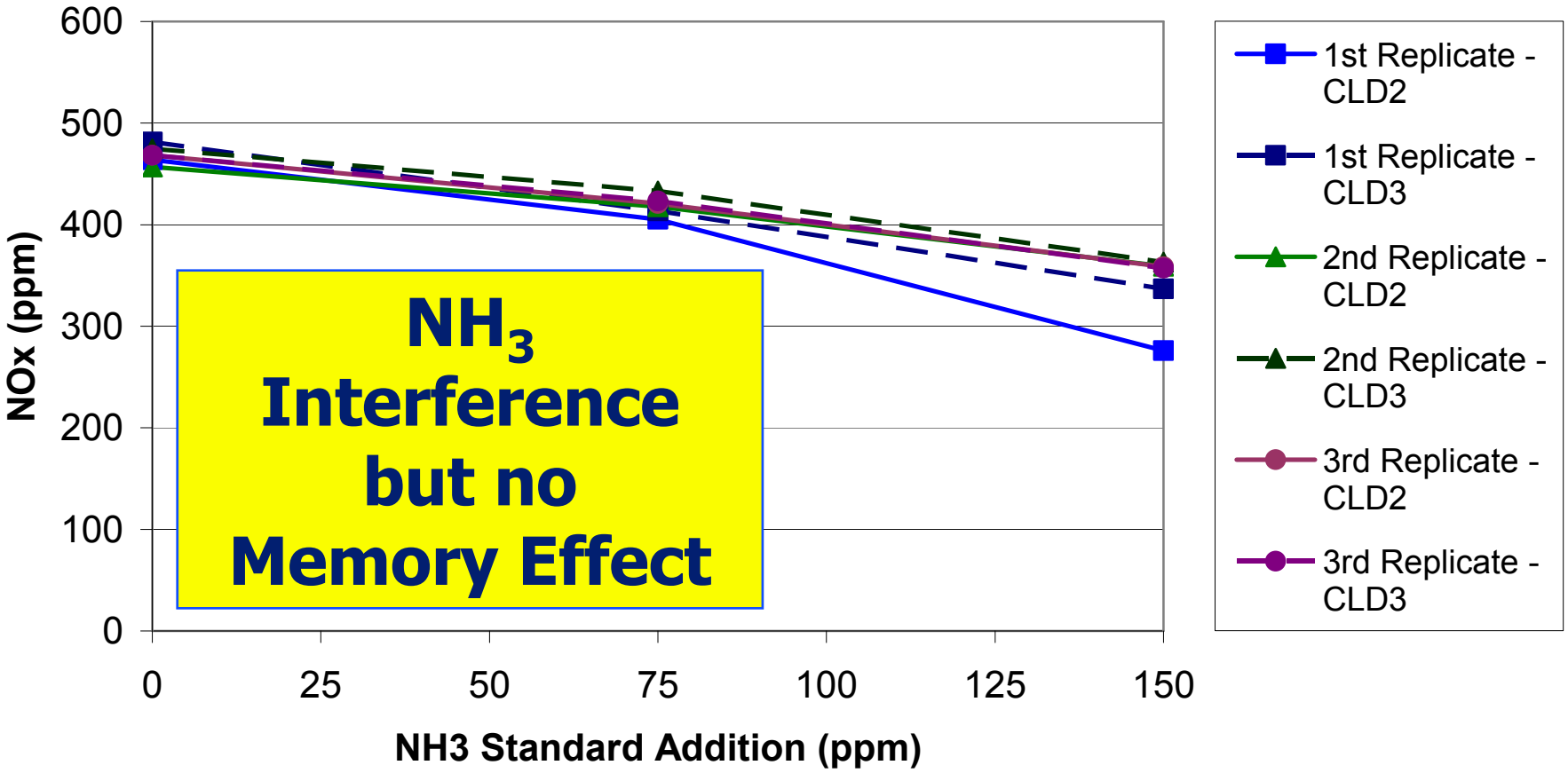
CLA NOx Response

- Regression equation from second replicate
- CLA with ***COM3*** catalyst
- NOx = 337 + 1.14 NOadd + 0.924 NO2add - 0.164 NH3add
- R^2 = 0.978
- All three coefficients are not zero at 95% confidence
- NOadd and NO2add slopes could be 1.0 within experimental confidence limits

95% Confidence Interval for Regression Coefficient (CLD - COM3)



CLD w/ Glassy Carbon Converter
Main Effect of NH3 on NOx Measurement



CLA NOx Response

- Regression equation from second replicate
- CLA with ***Glassy Carbon*** catalyst
- NOx = 269 + 1.08 NOadd + 0.982 NO2add - 0.728 NH3add
- R^2 = 0.986
- All three coefficients are not zero at 90% confidence
- Within experimental error, NO and NO_2 slopes could be 1.0
- Large NH_3 interference

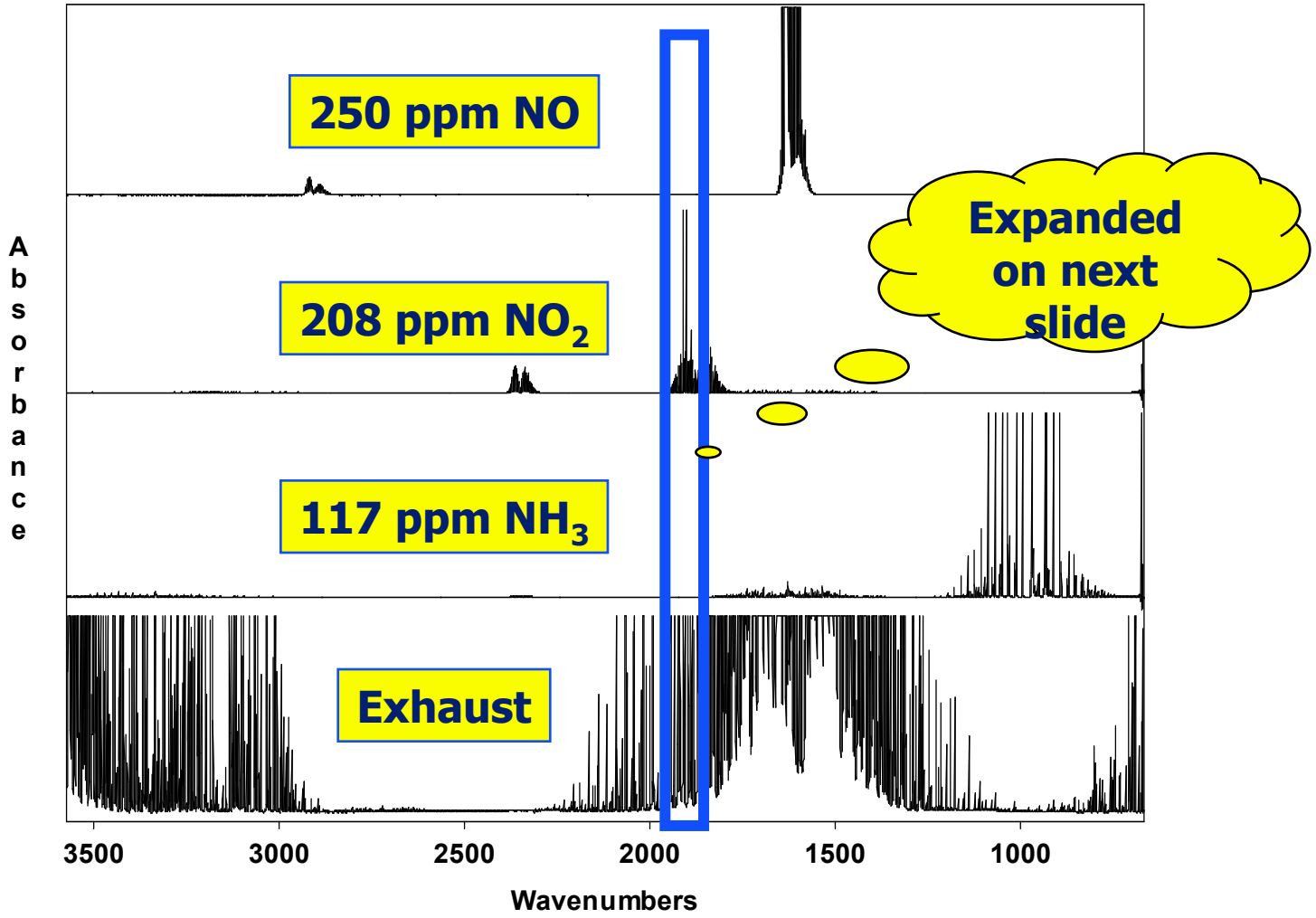
CLA Summary

- NOx measurement accuracy and repeatability when NH_3 is present is poor for the base COM3 converter.
- NOx measurement repeatability is much better with the updated glassy carbon converter, however a large NH_3 interference makes measurements inaccurate.
- CLA NOx measurements are not accurate when NH_3 is present in large concentrations.

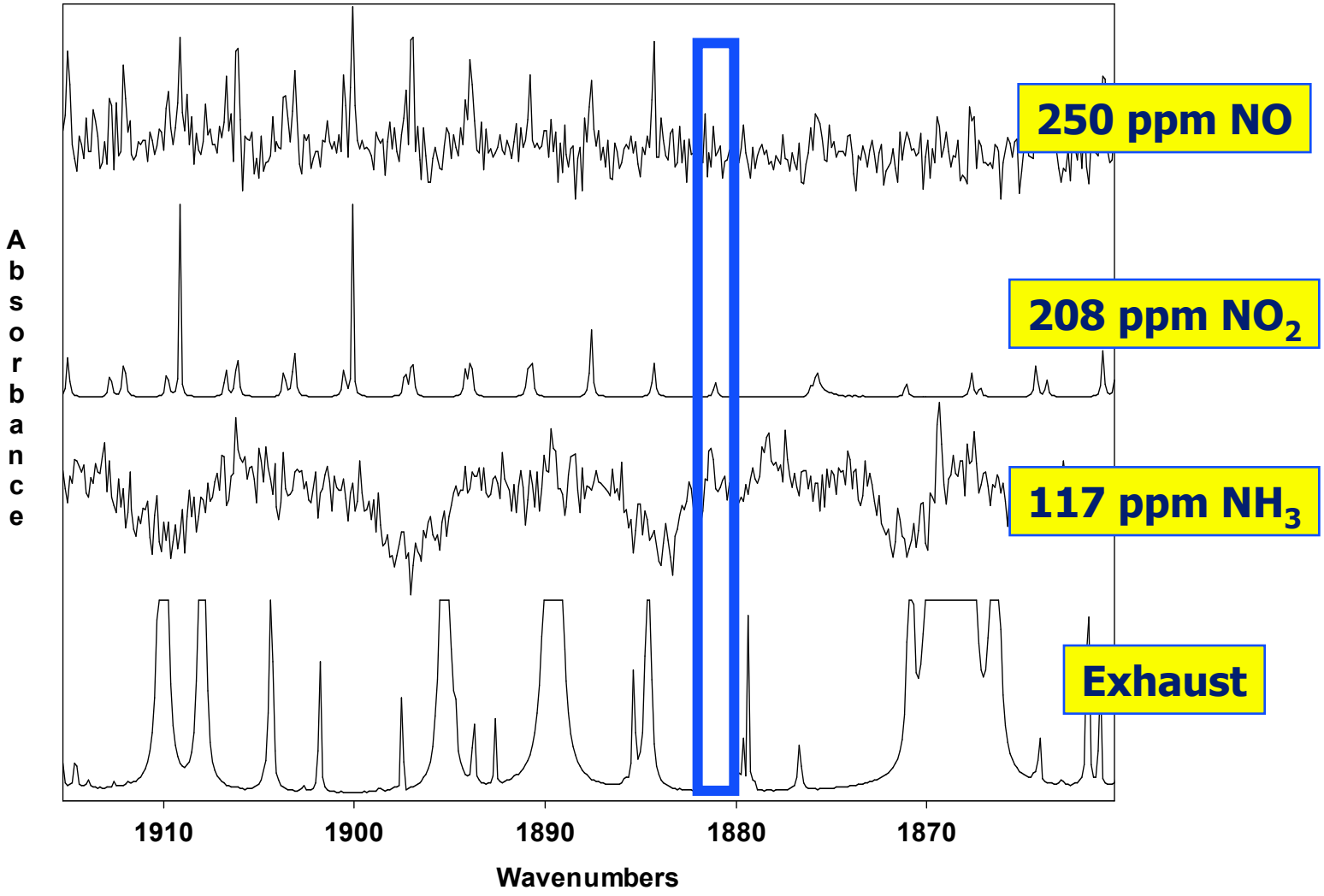
FTIR

- Fourier Transform Infrared Spectroscopy
- Commonly used gas analysis but potential issues
  - Interference from gases not included in the analysis set.
  - Saturation
  - Excessive Interference even with gases in the analysis set

Typical Exhaust Spectrum



Expanded Scale



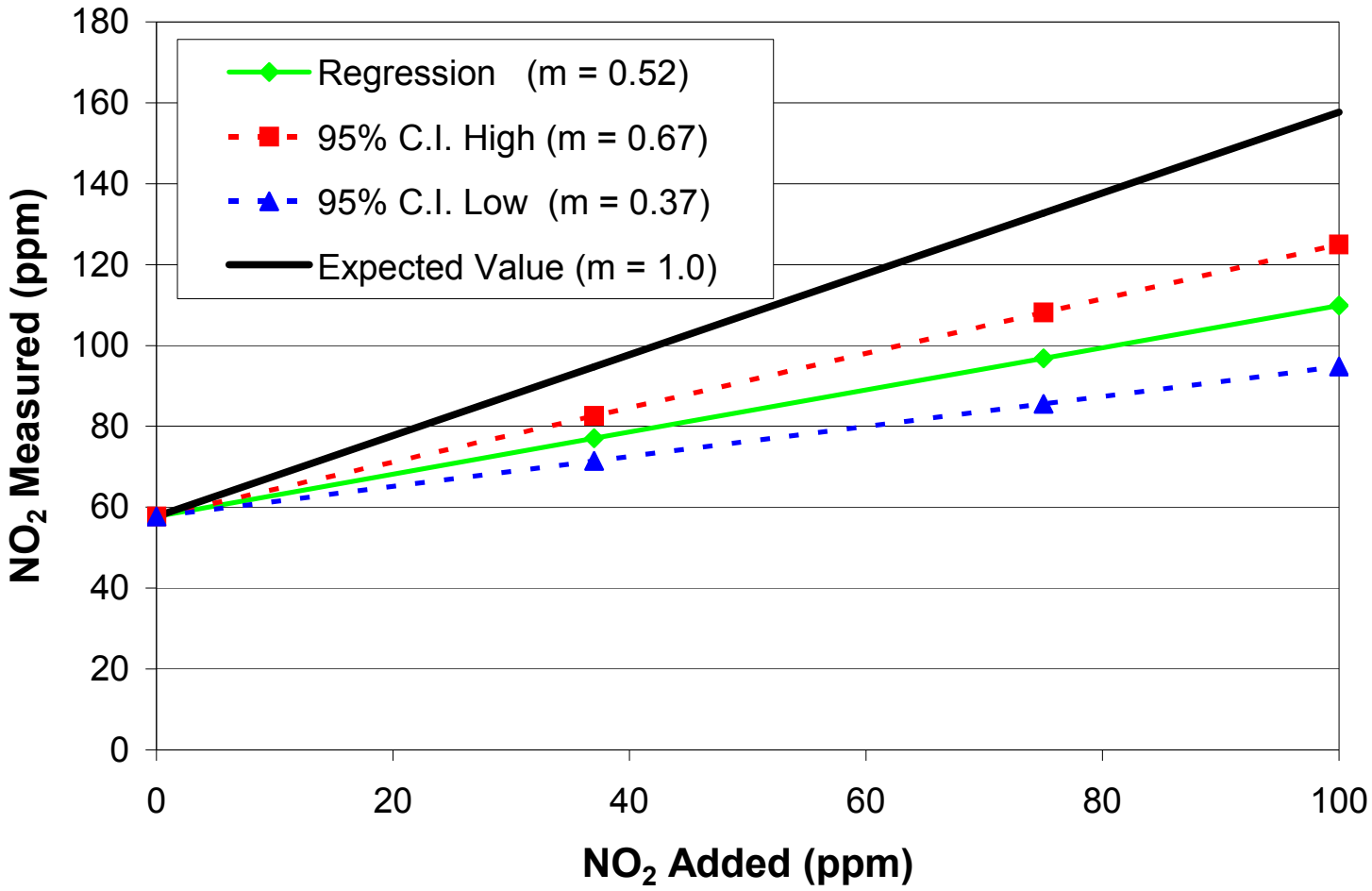
FTIR NO Response

- Regression equation from second and third replicates
- FTIR
- NO = 57.7 + 0.843 NOadd + 0.0156 NO2add - 0.0279 NH3add
- R^2 = 0.943
- NO and NH_3 coefficients are not zero at 90% confidence
- NO coefficient range includes 1; could give accurate NO
- NO_2 coefficient is *not* nonzero at 90% confidence
- No spectral saturation was present in the data

FTIR NO_2 Response

- Regression equation from second and third replicates
- FTIR
- NO_2 = 172 + 0.187 NOadd + 0.522 NO2add - 0.0141 NH3add
- R^2 = 0.839
- NO_2 coefficient is not zero at 90% confidence
- NO2 coefficient range *does not* include 1; NO_2 readings are inaccurate
- NO and NH_3 coefficients are *not* nonzero at 90% confidence

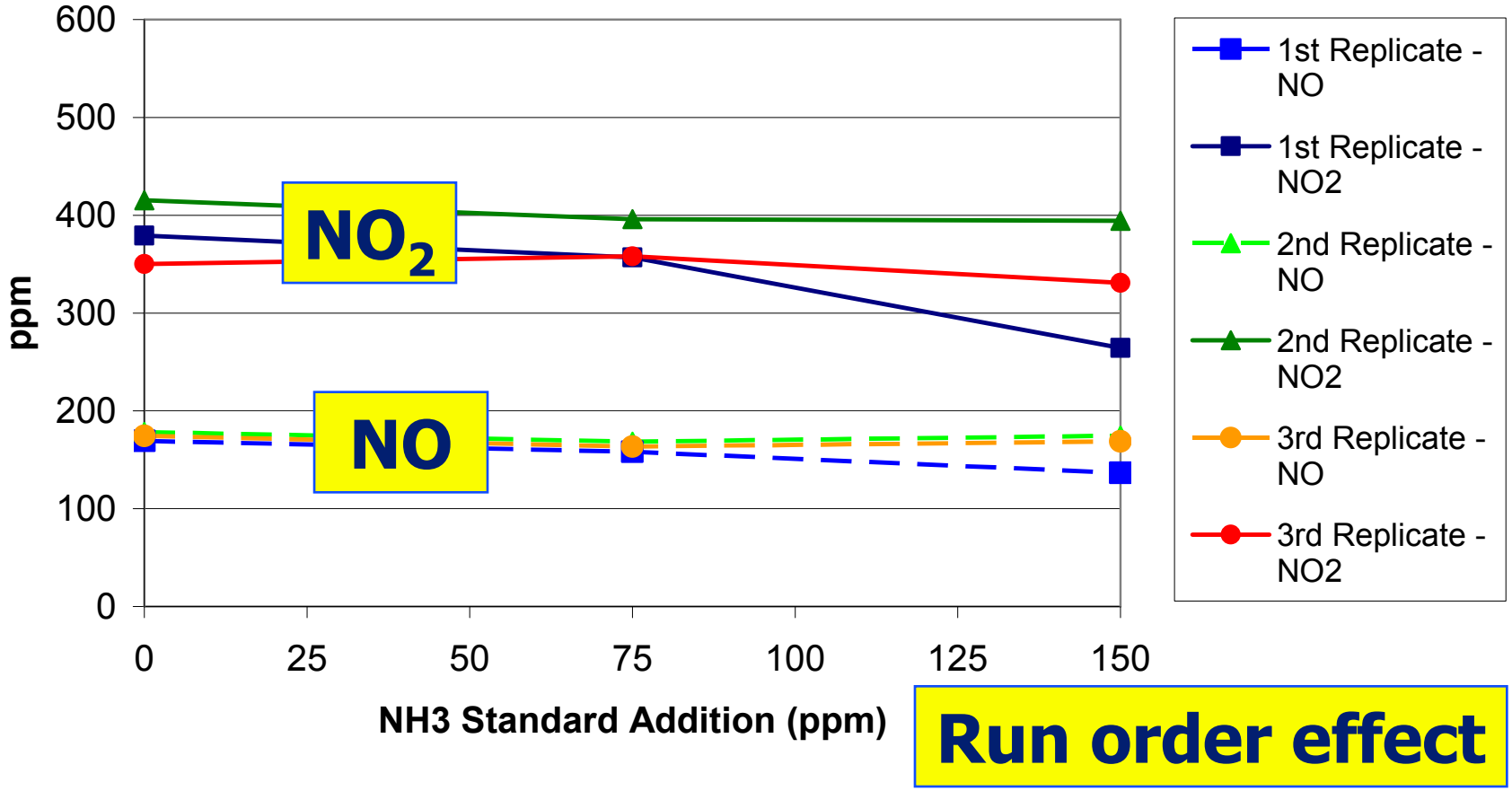
95% Confidence Interval for Regression Coefficient (FTIR NO_2)



FTIR Summary

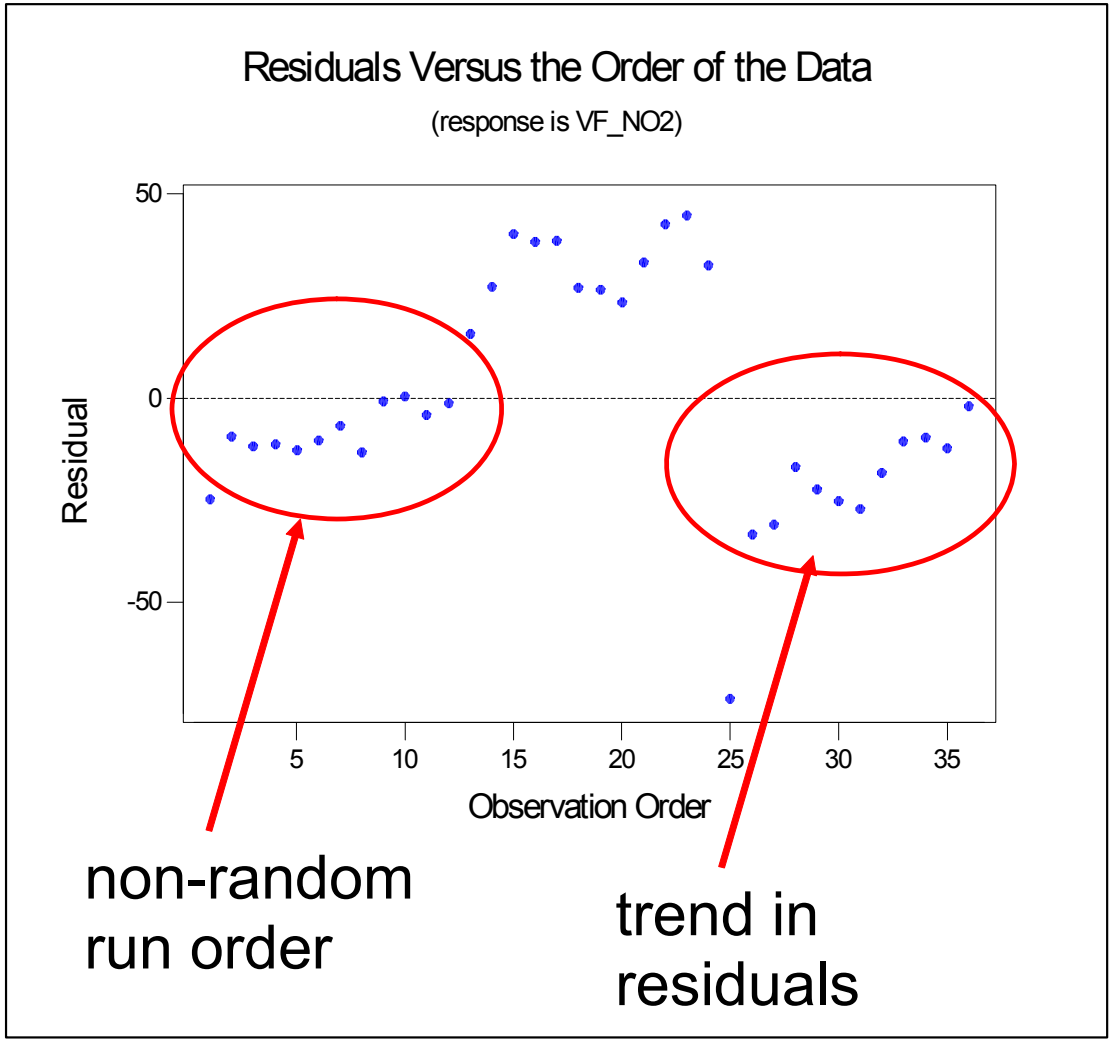
- NO measurements are not affected by NH_3, but *may* not match the known addition levels accurately
- NO_2 measurements are not affected by NH_3 level, and also *do not* match the known addition levels accurately
- Careful modification of the analysis method may well reduce the error in measurement
- Accurate measurement should be possible but requires careful user interaction

Mass Spectrometer
Main Effect of NH3 on NOx Measurement



Run order effect

Run Order Effects



- **10 micron orifice?**
- **Other contamination?**
- **Sample lines?**

CIMS NO Response

- Regression equation from second replicate
- CIMS
- NO = 105 + 1.21 NOadd + 0.0143 NO2add - 0.0194 NH3add
- R^2 = 0.953
- NO coefficient is not zero at 90% confidence
- NO coefficient range includes 1
- NO_2 and NH_3 coefficients are *not* nonzero at 90% confidence; small interferences exist

CIMS NO_2 Response

- Regression equation from second replicate
- CIMS
- NO_2 = 225 - 0.0682 NOadd + 1.13 NO2add - 0.131 NH3add
- R^2 = 0.992
- NO_2 and NH_3 coefficients are not zero at 90% confidence; interferences exist
- NO_2 coefficient range includes 1
- NO coefficient is *not* nonzero at 90% confidence

CIMS Summary

- Accurate measurements require regular instrument maintenance, apparently due to ammonium nitrate formation in the system
- NO measurements are not affected by NH_3, but may not match the known addition levels accurately
- NO_2 measurements are affected by NH_3 level, and additionally may not match the known addition levels accurately
- Careful recalibration and regular cleaning of the unit may well reduce the error in measurement, but is unlikely to remove the NH_3 effect.

Estimate of Engine NOx

- From Standard Addition Test, regression gives "zero addition" as estimate of engine out NOx
- Measurements do not agree!
- Note: CLAs are "dry" where FTIR and CIMS are wet; expect 7% higher reading when water is removed

Instrument	NO	NO_2	NOx
CLA COM3			337
CLA GC			269
FTIR	58	172	230
CIMS	105	225	330

Experiment Summary

- Chemiluminescent analyzers do not provide accurate measurement of NOx when NH_3 is present in engine exhaust gas.
- FTIR may provide accurate measurements if analysis methods are developed to provide adequately low interference.
- Chemical ionization mass spectroscopy may provide accurate measurements, although the unit tested appears to need significant cleaning and maintenance to do so.
- No presently available measurement provides accurate and robust measurement of NO, NO_2, NOx, and NH_3 when NH_3 is present in large quantity.
- Recommend development of an NH_3 scrubber