

Comparison of Ammonia Continuous Measurement Techniques from an SCR Vehicle

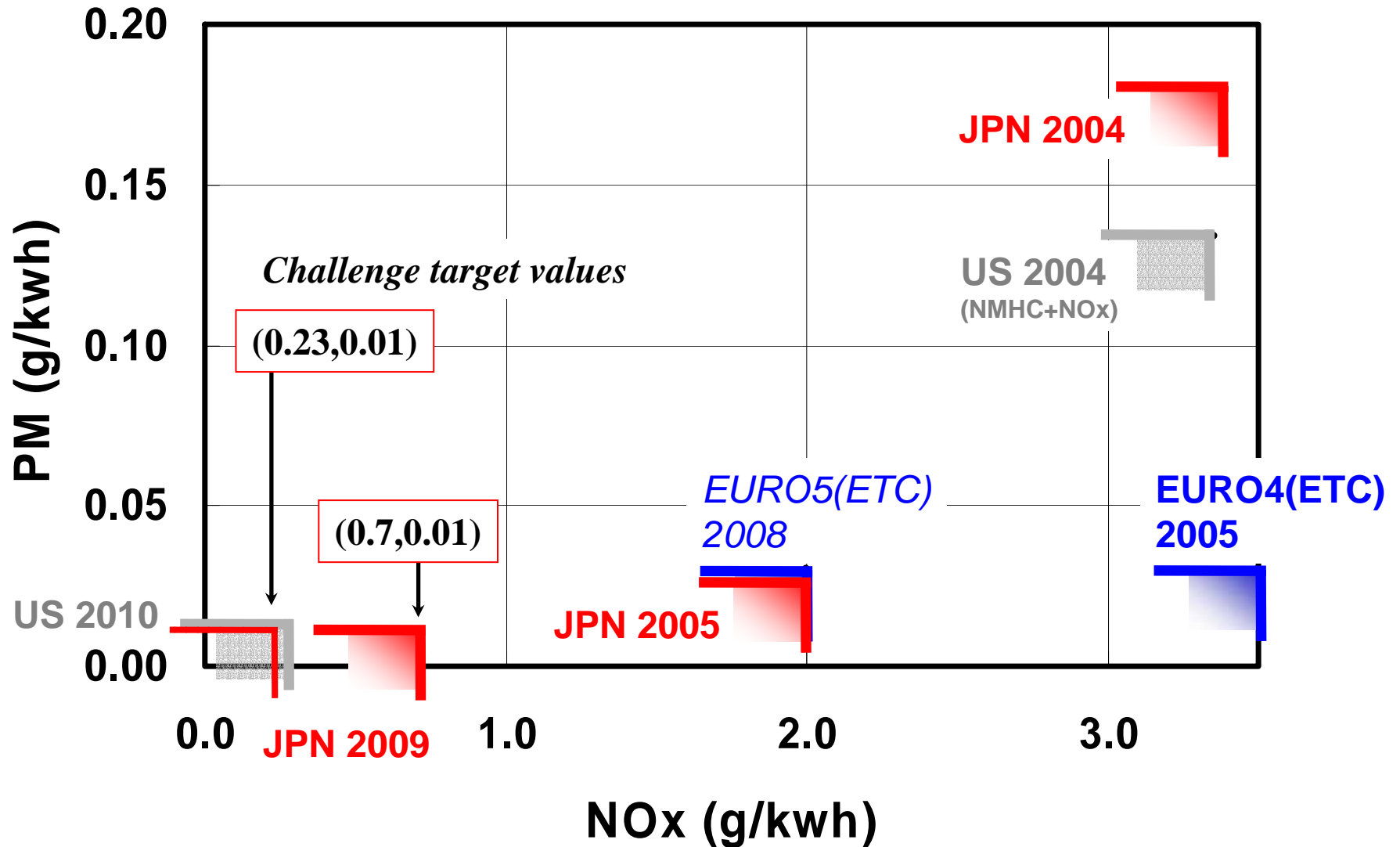
Eighth CLEERS Workshop
May 19, 2005

Hajime Ishii, Hisakazu Suzuki
Environment Research Department
National Traffic Safety and Environment Laboratory, JAPAN

Presentation overview

- 1. Background (Emission regulation)**
- 2. Feasibility study of SCR vehicles**
- 3. Ammonia measurement test**
- 4. Activated and de-activated catalyst test**
- 5. Conclusion**

History of emission regulation

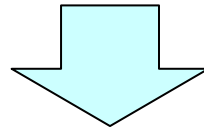


What is “Challenge Target Values” for HD vehicles?

- Higher target values have been established with the expectation of further technological progress.

(Subject)

- Developments of NO_x reduction performance at low-temp.
- Future prospect of practical utility of HCCI or new technology.
-e.t.c.



- After verifications have been made around 2008, final decision will be made on the necessity of new target values and the achievement year.

(Reference: Kubota H., JSAE 2005 Spring Meeting)

Presentation overview

- 1. Background (Emission regulation)**
- 2. Feasibility study of SCR vehicles**
- 3. Ammonia measurement test**
- 4. Activated and de-activated catalyst test**
- 5. Conclusion**

Test vehicles with SCR system

1999 Regulation + SCR system (no engine adjustment)

VehicleA



VehicleB



Vehicle C



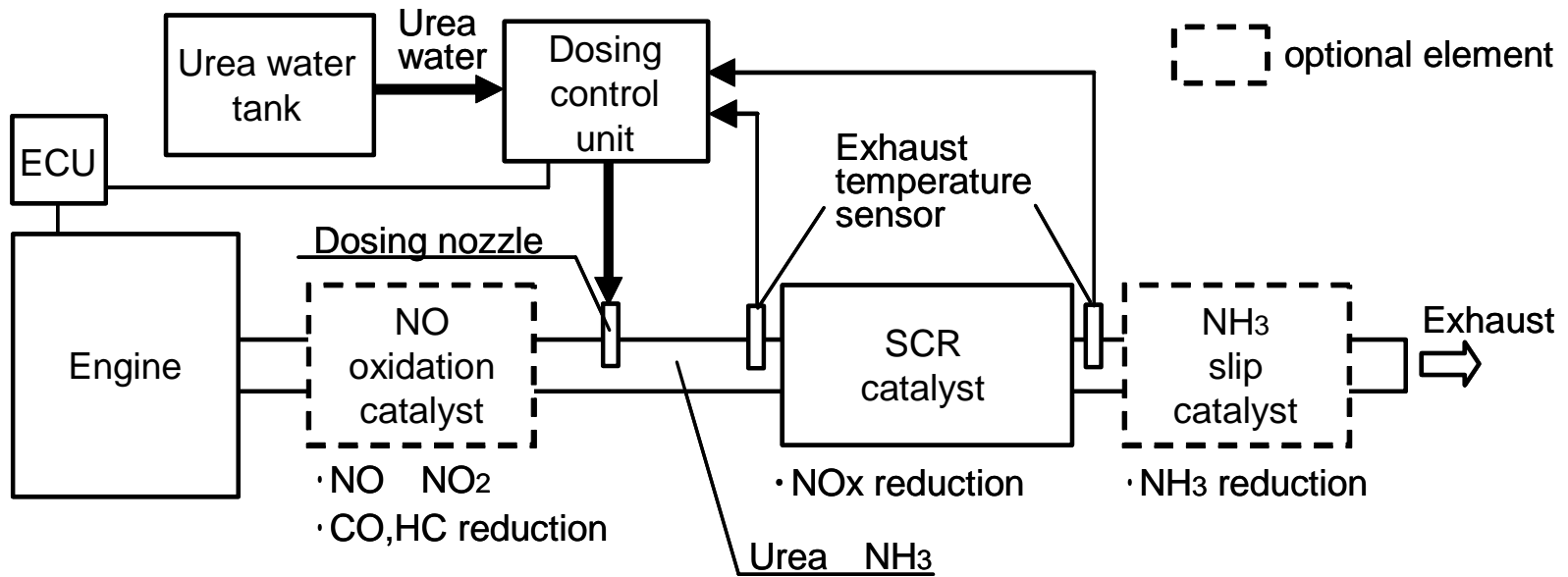
Vehicle D



(Reference: JARI, "Research Development of Exhaust Gas Aftertreatment System, 2003")

Specification of The Urea SCR System

System / Vehicle	A	B	C	D
NO oxidation catalyst Volume	5.1L	-	8.5L	8.5L
SCR catalyst Volume	Vanadium 46.4L	Vanadium 30.2L	Vanadium 53.4L	Zeolite 17.0L
NH ₃ slip catalyst Volume	-	-	7.0L	8.5L
Urea water tank	Resin 50L	Resin 50L	Resin 50L	Stainless steel 15L



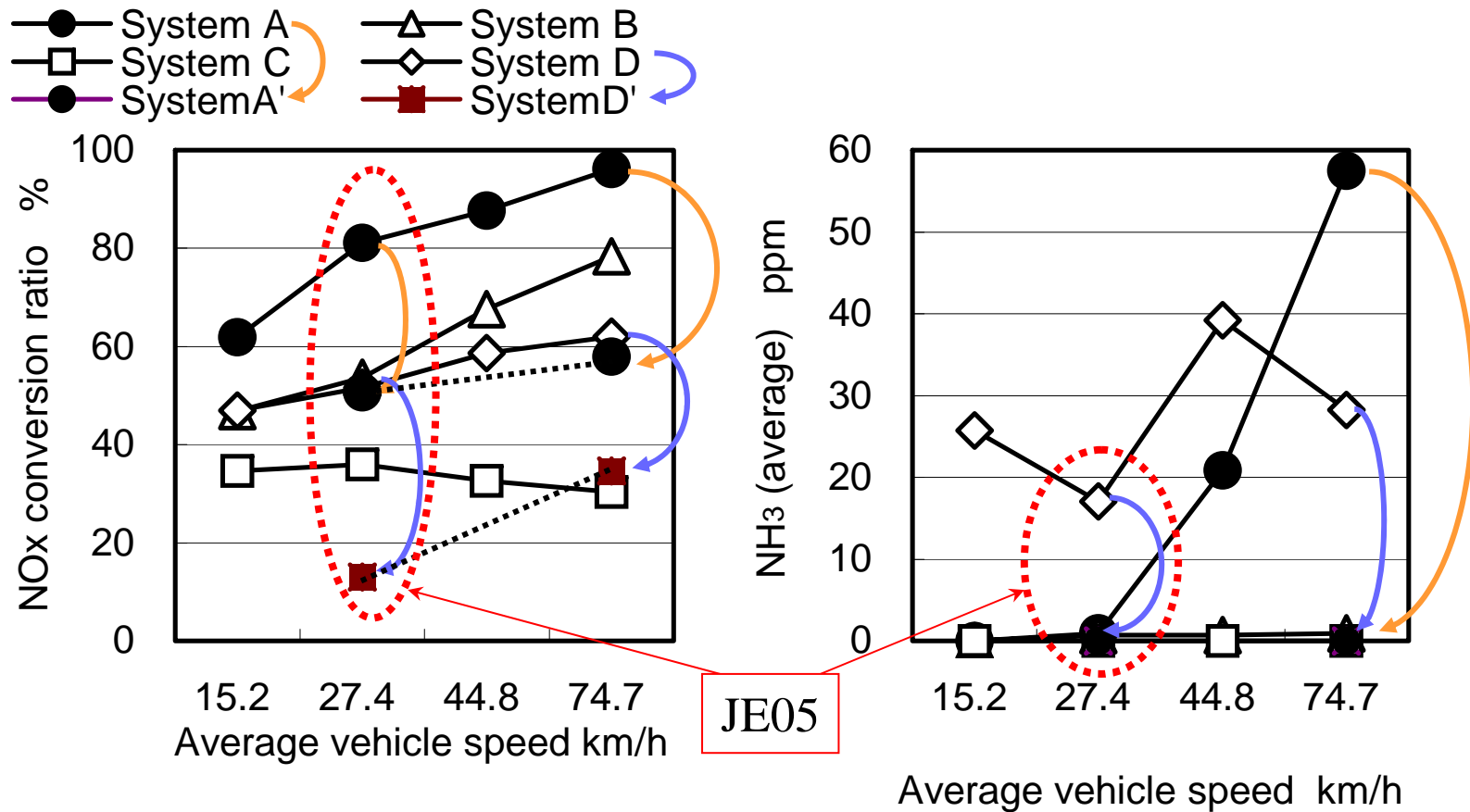
SAE 2004-01-1944

D13 Emissions Performance

		Emission (g/kWh)				
		CO	HC	NOx	PM	CO ₂
System A	Base	1.46	0.31	4.65	0.17	847
	w/SCR	0.03	0.01	1.76	0.17	844
	Conversion	98.1	95.8	62.1	-2.9	0.4
System B	Base	1.07	0.42	4.29	0.21	783
	w/SCR	1.69	0.06	1.28	0.22	788
	Conversion	-56.9	86.7	70.2	-7.2	-0.7
System C	Base	1.18	0.30	5.34	0.03	781
	w/SCR	0.20	0.05	1.87	0.02	801
	Conversion	82.7	82.4	65.1	29.4	-2.5
System D	Base	0.98	0.14	4.87	0.20	827
	w/SCR	0.00	0.01	2.11	0.23	839
	Conversion	99.9	94.3	56.7	-16.7	-1.5

SAE 2004-01-1944

NOx Conversion Ratio and NH3 Slip



Systems A' and D' : After adjustment of urea injection in transient test 2 and 4

Conclusion-1 of the feasibility study

- The maximum NO_x conversion ratio of the urea SCR system developed was 70% under the steady-state test of D13 mode cycle, but decreased during the transient driving cycle. This must be significantly improved in order to apply for future emission regulation, especially under low-speed operating conditions.
- NH₃ slip under the D13 and the transient cycle was eliminated by adjusting the urea injection, but the trade off between NO_x conversion efficiency and NH₃ slip has to be improved in order to put the urea SCR system to practical use.

SAE 2004-01-1944

Presentation overview

- 1. Background (Emission regulation)**
- 2. Feasibility study of SCR vehicles**
- 3. Ammonia measurement test**
- 4. Activated and de-activated catalyst test**
- 5. Conclusion**

Necessity of NH₃ measurement

Ammonia

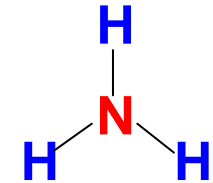
- to a human

- TWA (Time Weighted Average) defined by ACGIH (American Conference of Governmental Industrial Hygienists) is 25ppm, which is the same as CO

- from a vehicle

- NH₃ formation reaction is taken place on catalyst, when NO_x is reduced in rich condition

- NH₃ slips when urea solution is injected to much in urea SCR system



We need to understand accurate measurement method of NH₃

NH₃ measurement of SCR vehicle

Object: Quantification of temporal and total NH₃ emission under transient condition

Characteristics of NH₃

- readily soluble in water

 - large error caused by water vapor condensation in exhaust gas

- reaction to other components in exhaust gas

 - easily stagnant in a sample line

Therefore, it is difficult to measure NH₃ by CVS system.

To fulfill above object, heated direct line sampling is necessary in measurement test.

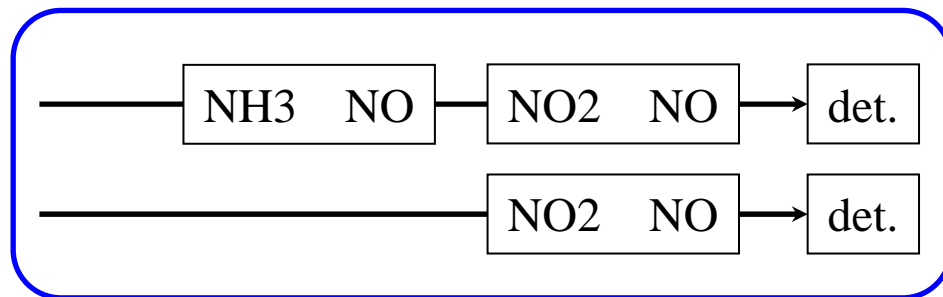
NH₃ measurement of SCR vehicle

- ◆ **Comparing and evaluating four continuous NH₃ measurement systems**
- ◆ **Understanding accuracy and characteristics of practical requirements by measuring heavy duty truck equipped with urea SCR system**

Measurement system (1)

Dual Chemiluminescence detector (Dual CLD=DCLD)

- Two CLD detectors
- One has a converter which converts NH₃ to NO_x
- (NH₃+NO_x)-(only NO_x) =NH₃



Advantage: reliability of NO_x measurement

Disadvantage: affected by NO_x concentration level

Full scale at the experiment: 1,000ppm



Measurement system (2)

Soft Ionization Mass Analyzer

(MS)

- Identifying components by mass information of electrical charge and molecular weight, after ionizing materials
- Generally batch measurement type, focusing on accuracy rather than response

Advantage : High accuracy

Disadvantage : Cost

Full scale at the experiment : 100ppm



Measurement system (3)

Fourier Transform Infrared spectroscopy (FTIR)

Analyzing magnitude of each components absorption in infrared band by Fourier transform

Advantage : real time, continuous and simultaneous multi components measurement

Disadvantage : cross sensitivity

Full scale at the experiment : 200ppm



Measurement system (4)

Diode Laser Spectrometry (LDS)

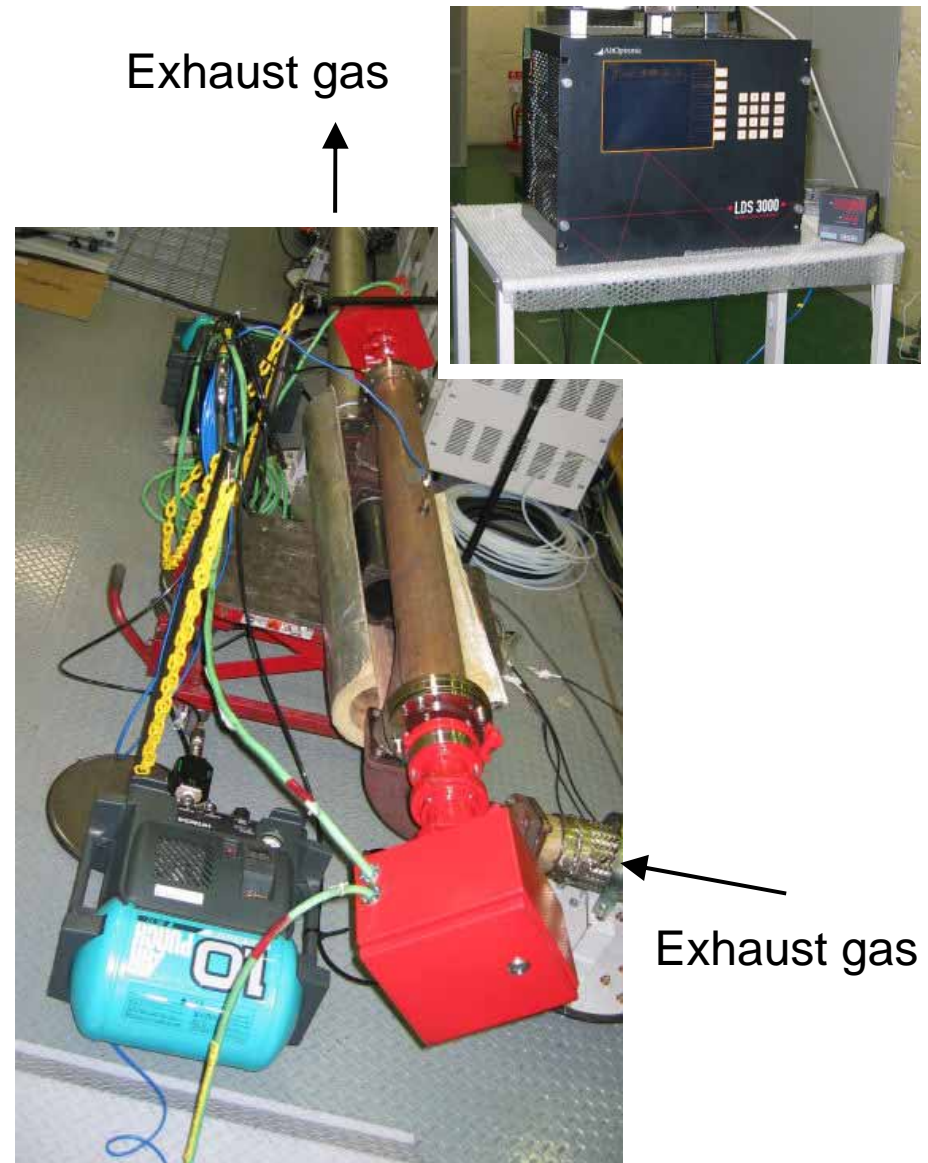
Measuring absorption of NH_3

- Less cross sensitivity of other components NH_3
- exhaust pipe itself works as test cell, improving response by avoiding adsorption

Advantage: Response

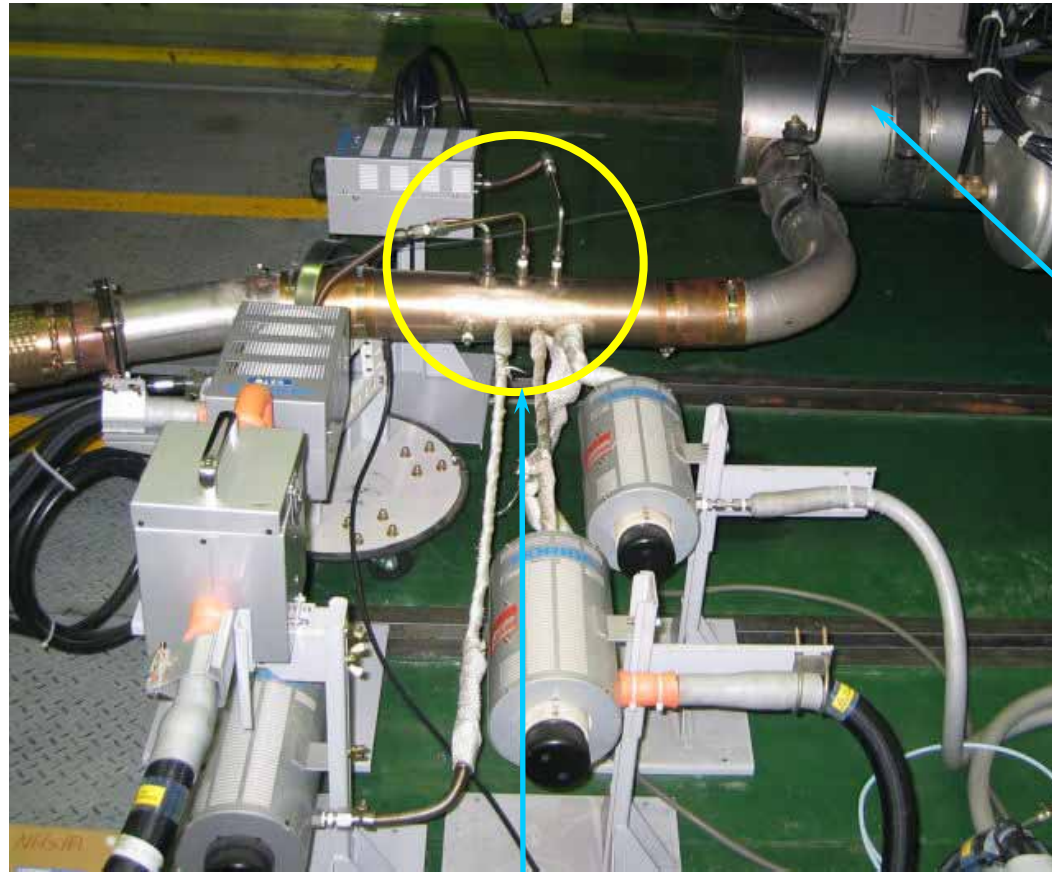
Disadvantage: Exhaust pipe modification

Full scale at the experiment: 200ppm



Sampling NH₃

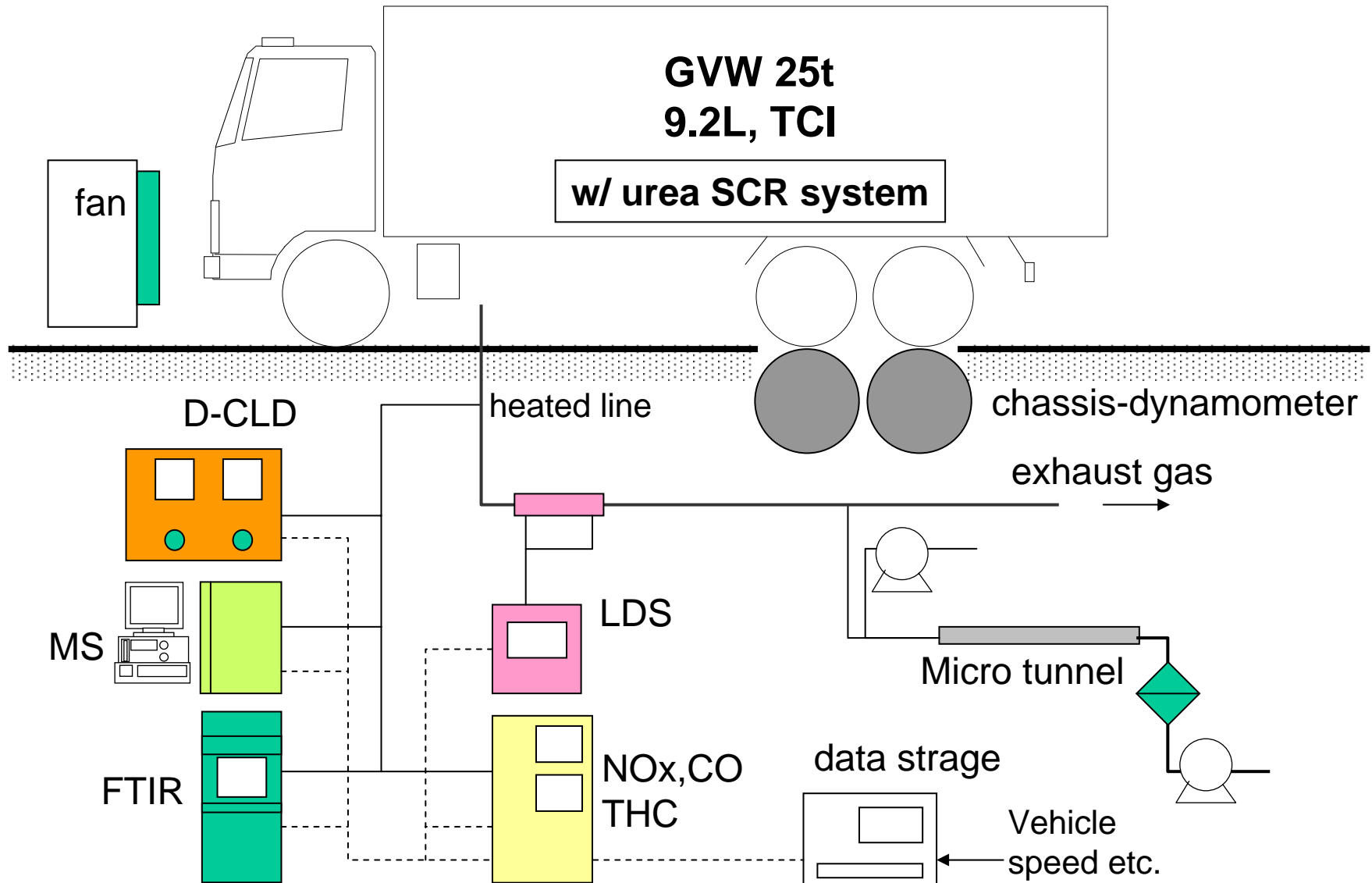
Exhaust gas



Catalyst

Sample probes of DCLD, MS, and, FTIR are located within 30cm (one foot) from the tail pipe.

Experiment system



Materials for Vehicle's Catalyst

About exhaust gas measures for in-use vehicles

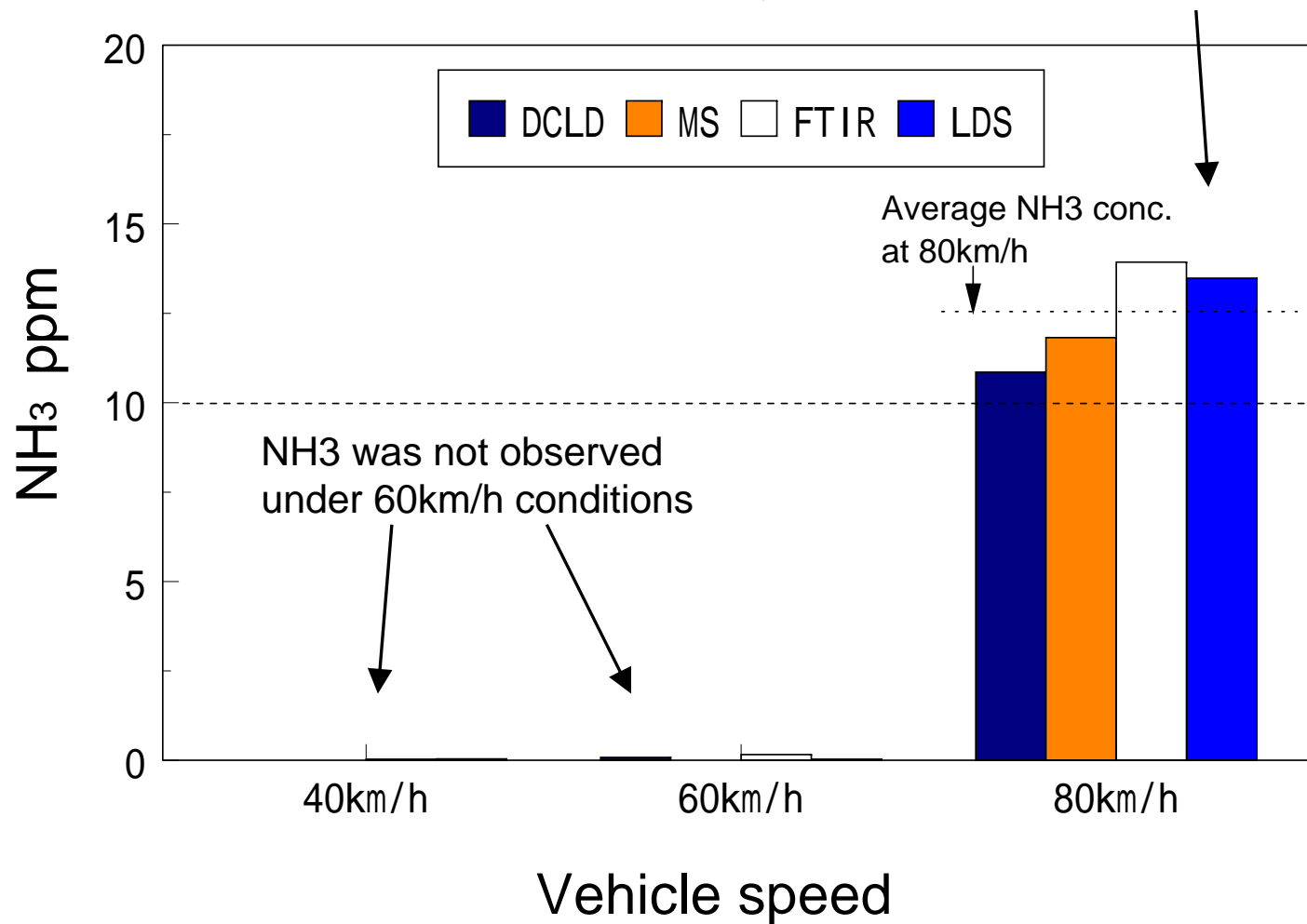
“Some metals used for catalyst such as vanadium, chromium, mangan, cobalt, nickel and copper have possibility of secondary disaster. These metallic components should not be emitted in the atmosphere.”

(12 of October, 1972,

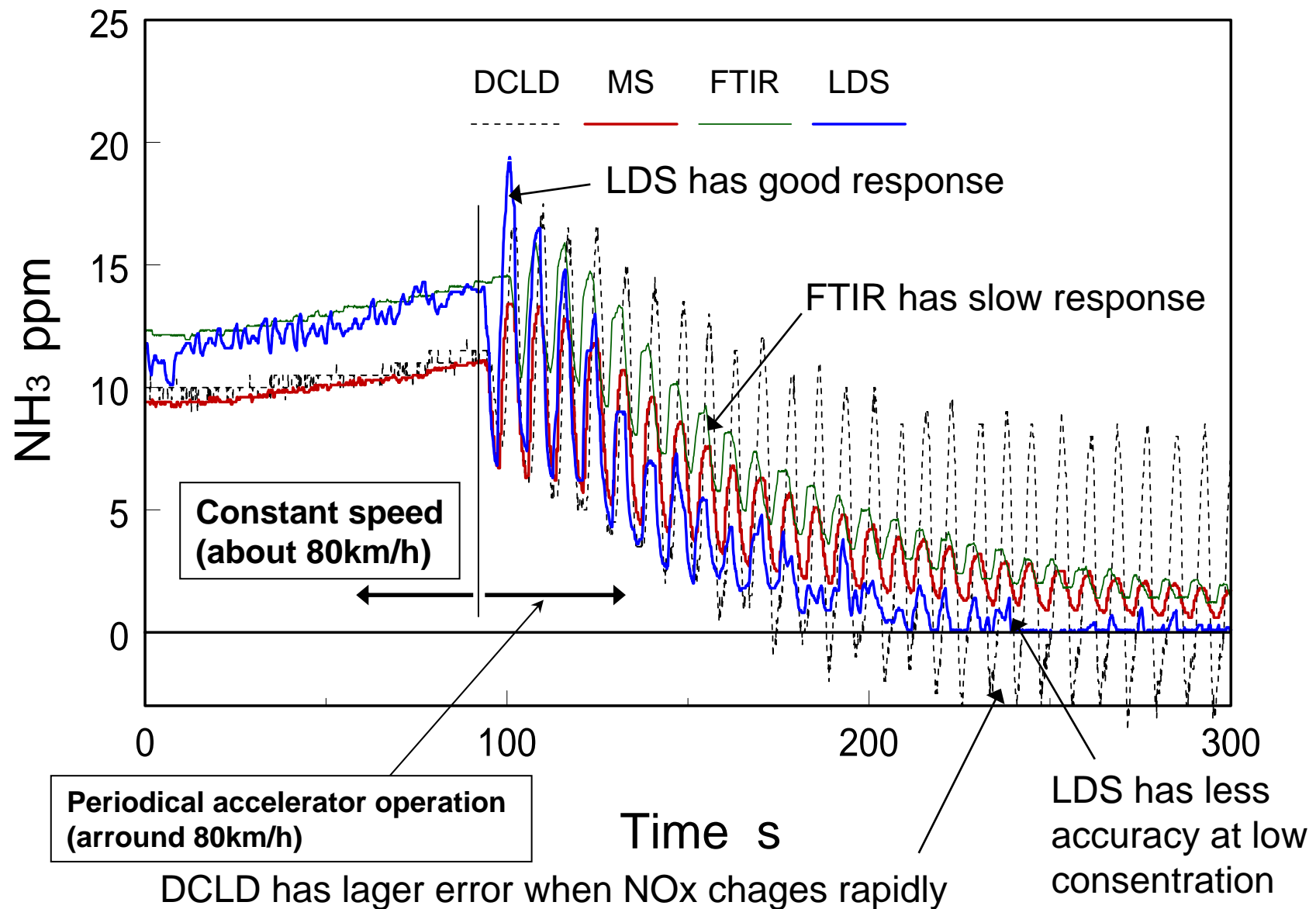
Exhaust Gas Measures WG, Motor Vehicle Division, Transport Technology Council, Ministry of Transport)

Comparison of NH₃ concentration (constant speed)

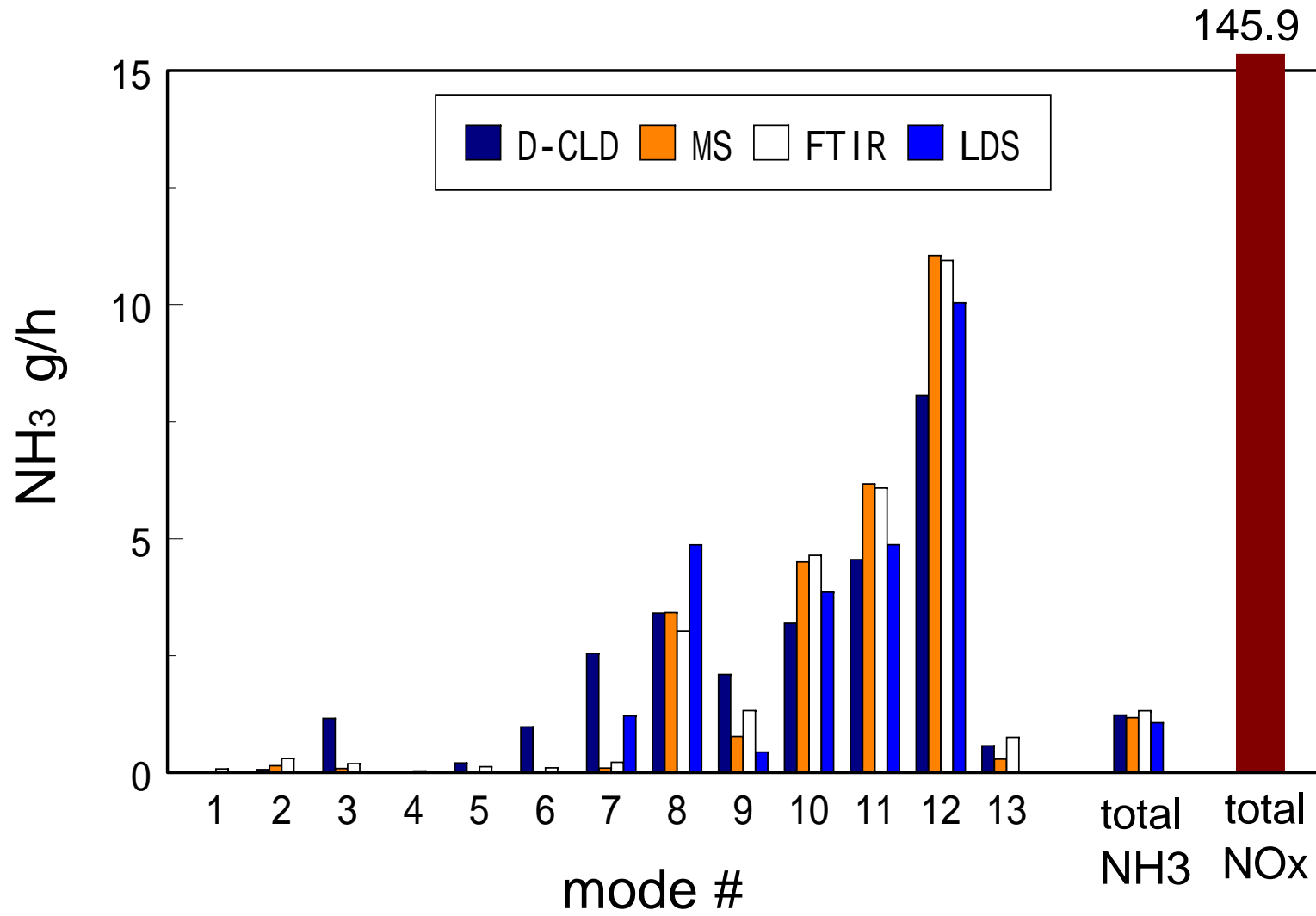
Deviations are within about 1% of each system's full scale



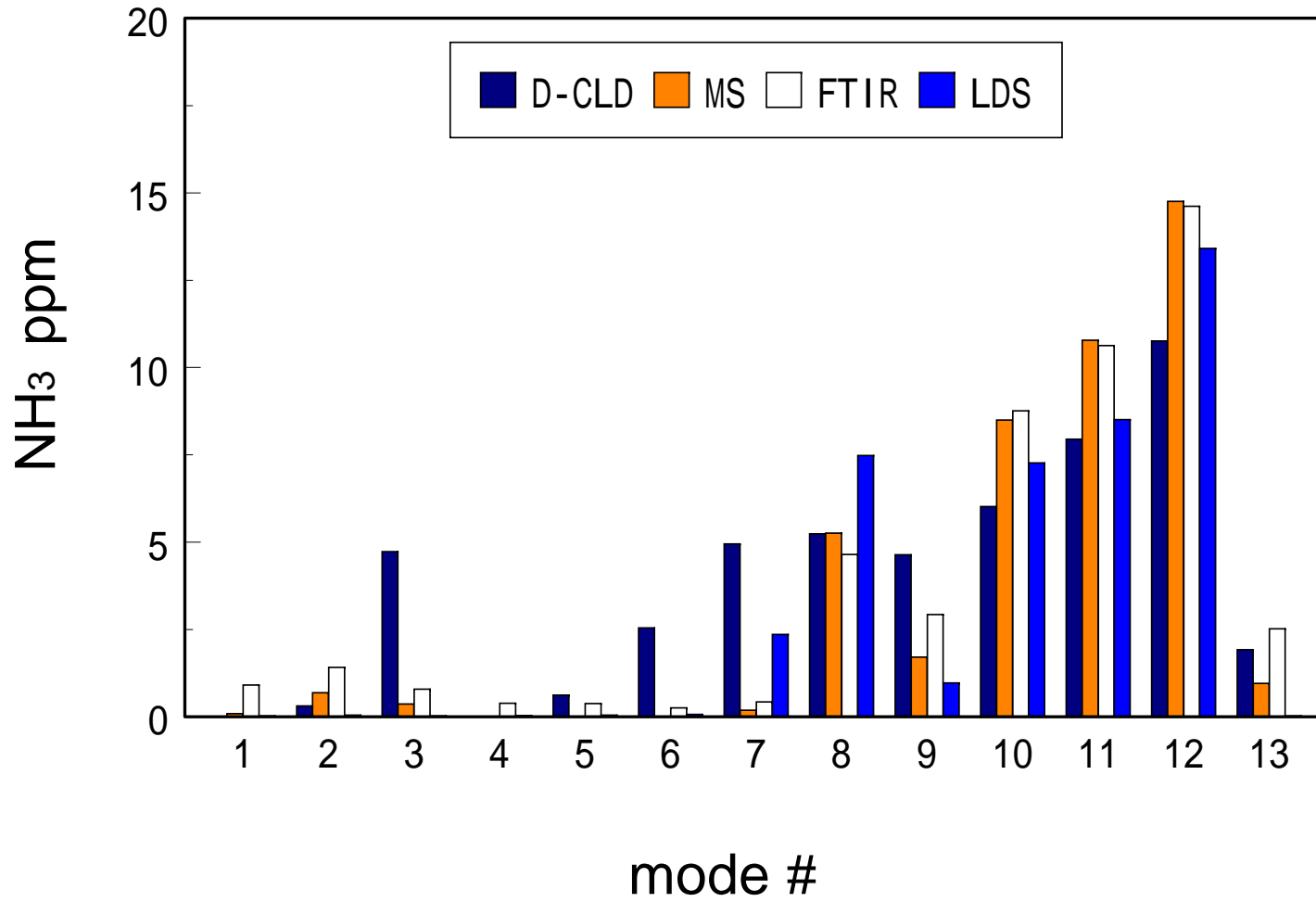
NH₃ measurement accuracy and response



NH3 mass at D13 mode test

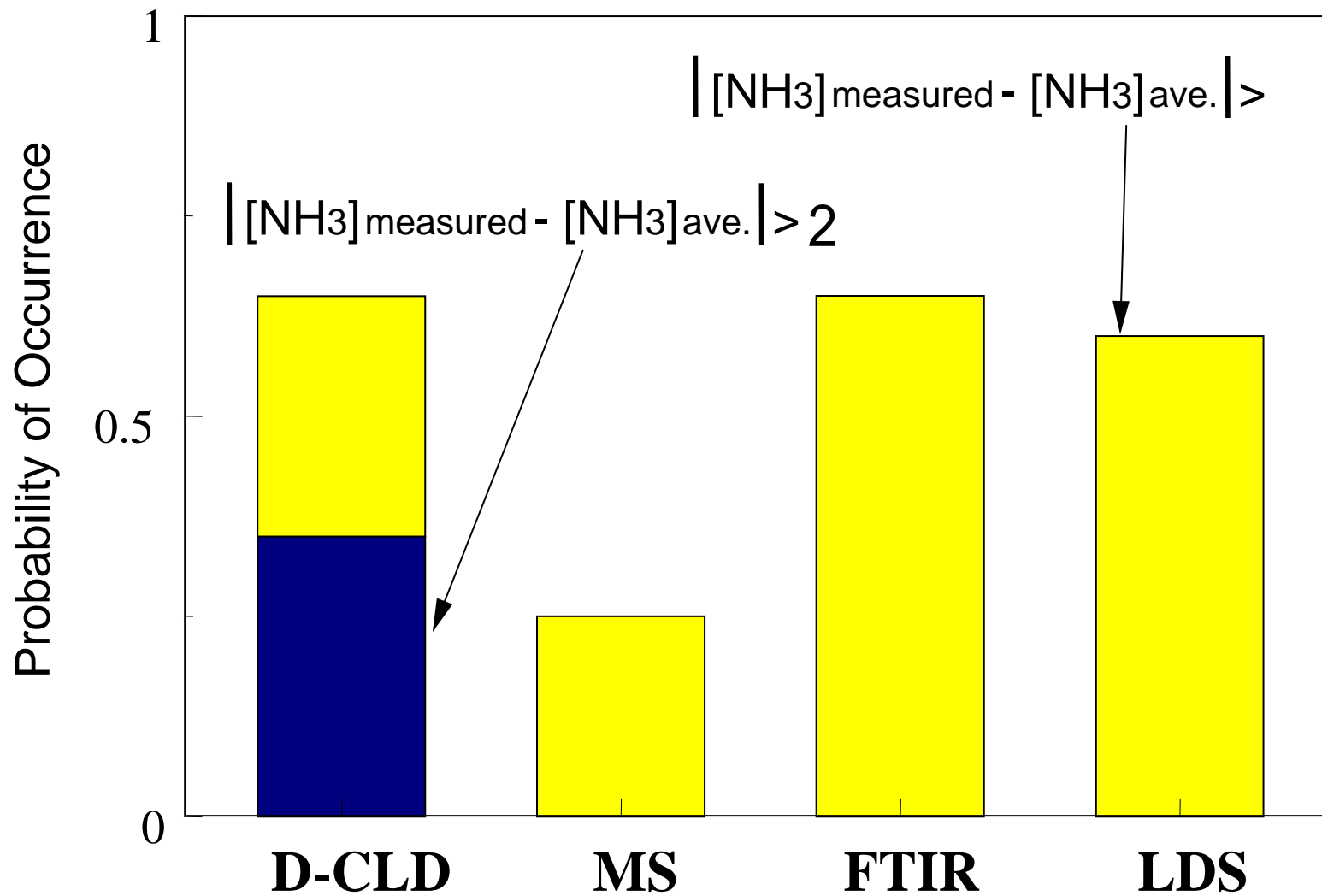


NH₃ concentration at D13 mode test



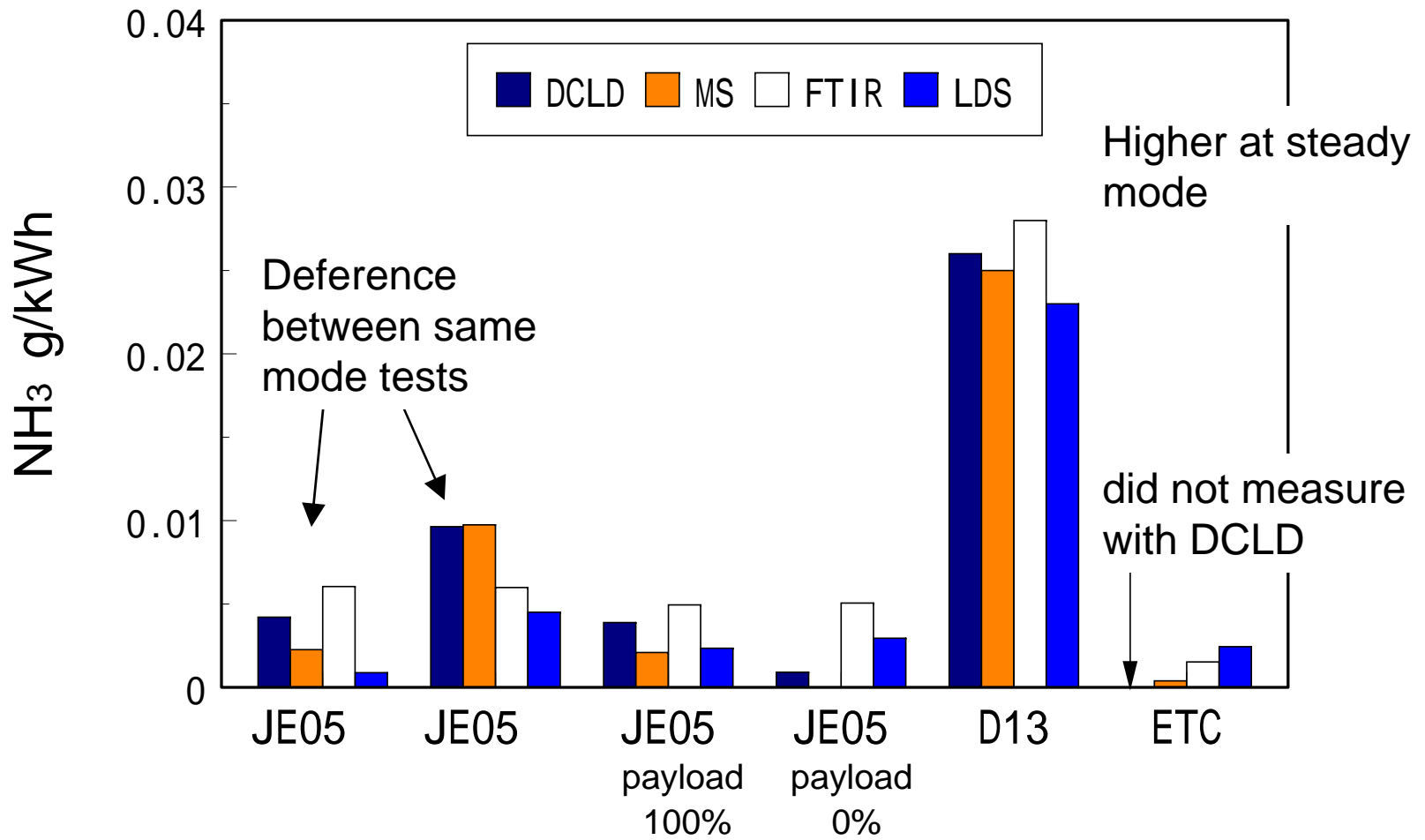
Sensitivity analysis of measurement systems

D13 mode

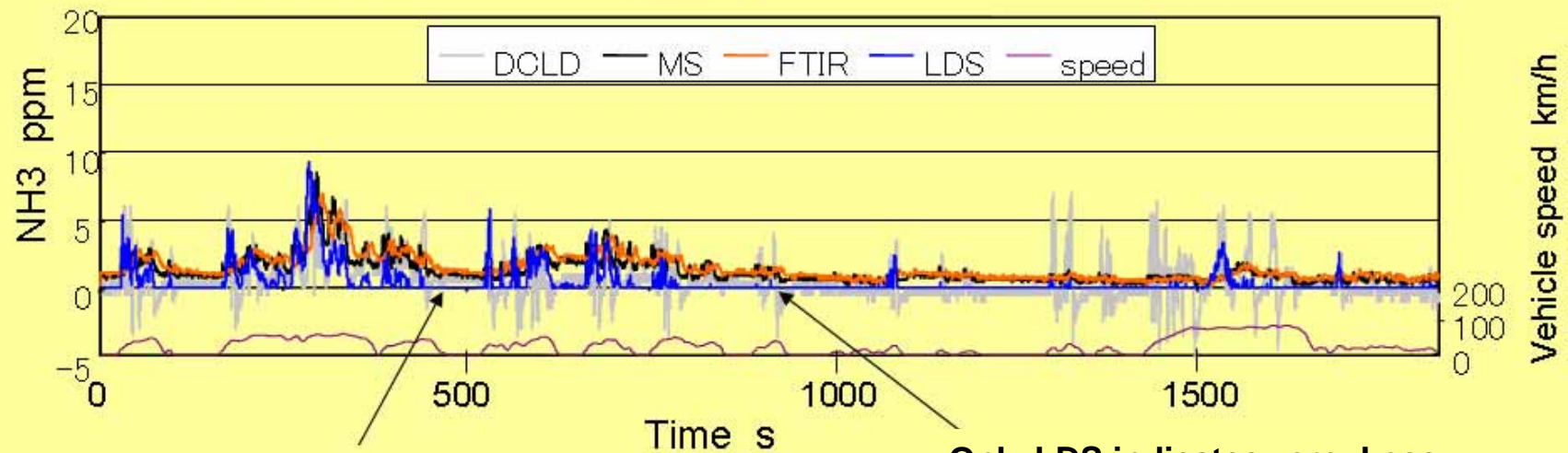
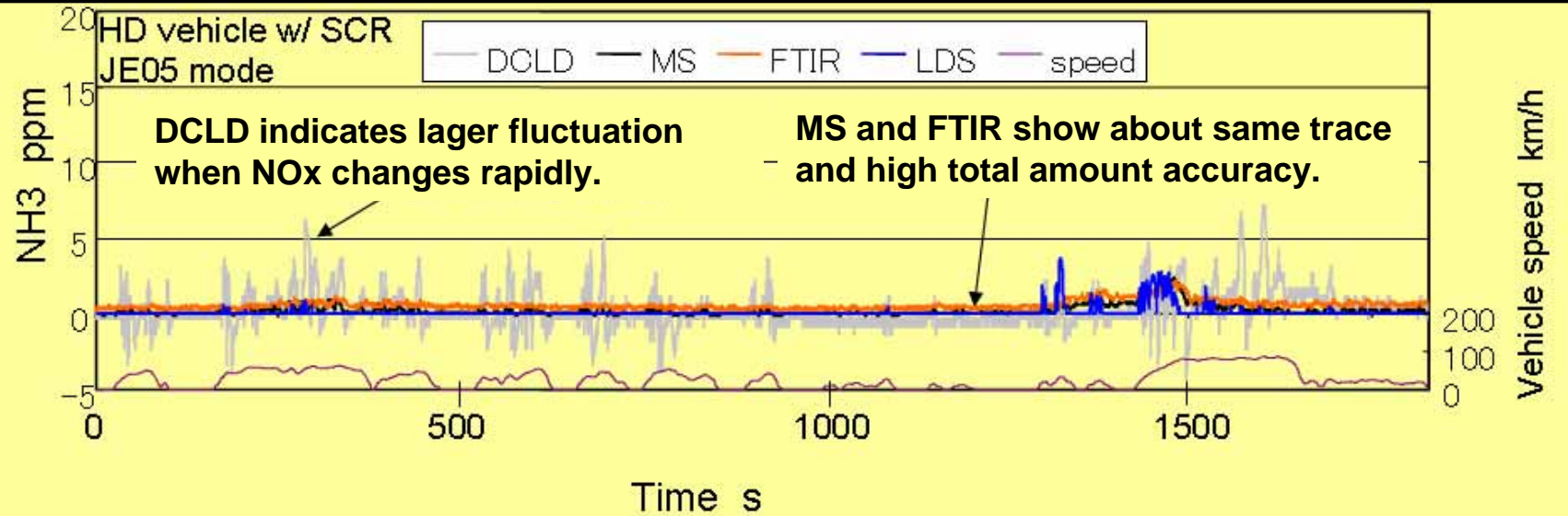


NH3 emission at various mode

Note that Japanese 2005 NOx regulation is 2.0g/kWh !



NH3 concentration comparison (JE05 mode)



Catalyst temperatures and NO_x emissions are about same but NH₃ emissions are deferent.

→ Need some discussion about Pre-conditioning

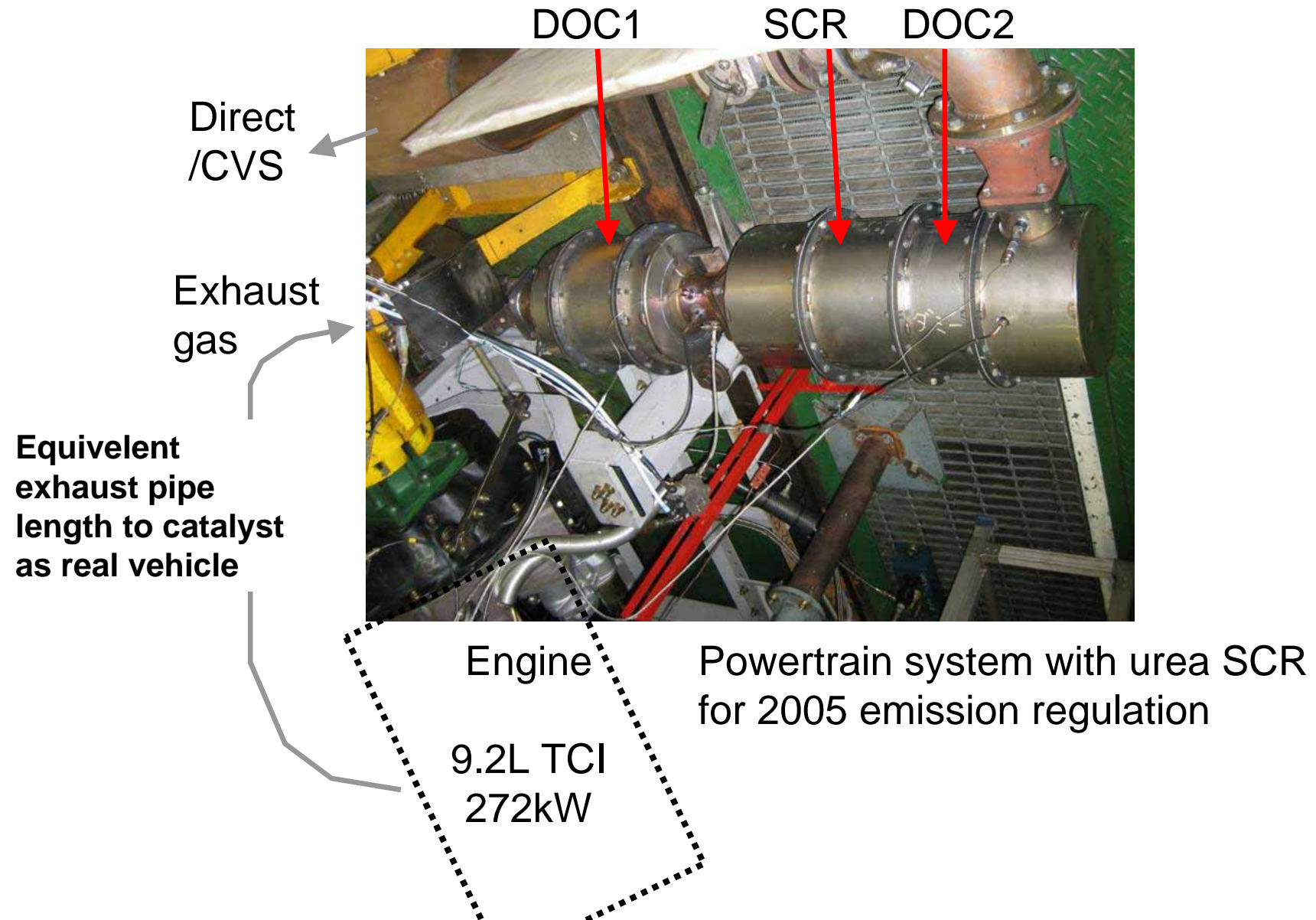
Presentation overview

- 1. Background (Emission regulation)**
- 2. Feasibility study of SCR vehicles**
- 3. Ammonia measurement test**
- 4. Activated and de-activated catalyst test**
- 5. Conclusion**

Engine specification

Name	MD92
Type	DI, TCI
Cylinder #, valve type	Inline 6, OHC
Displacement L	9.2
Max. Power kW/rpm	272/2200
Max. Torque Nm/rpm	1470/1400
Injection system	Common rail
After treatment device	Urea SCR (w/ DOC)
Vehicle Weight kg	16640 (half payload)

Experiment system



Catalyst specification and setting conditions

	DOC1	SCR	DOC2
Size L	8.5	8.5	5.7
Main Component	Pt	Fe (non Vanadium)	Pt

Condition ID	DOC1	SCR	DOC2
A			
B		dummy	
C			dummy
D	dummy	dummy	dummy

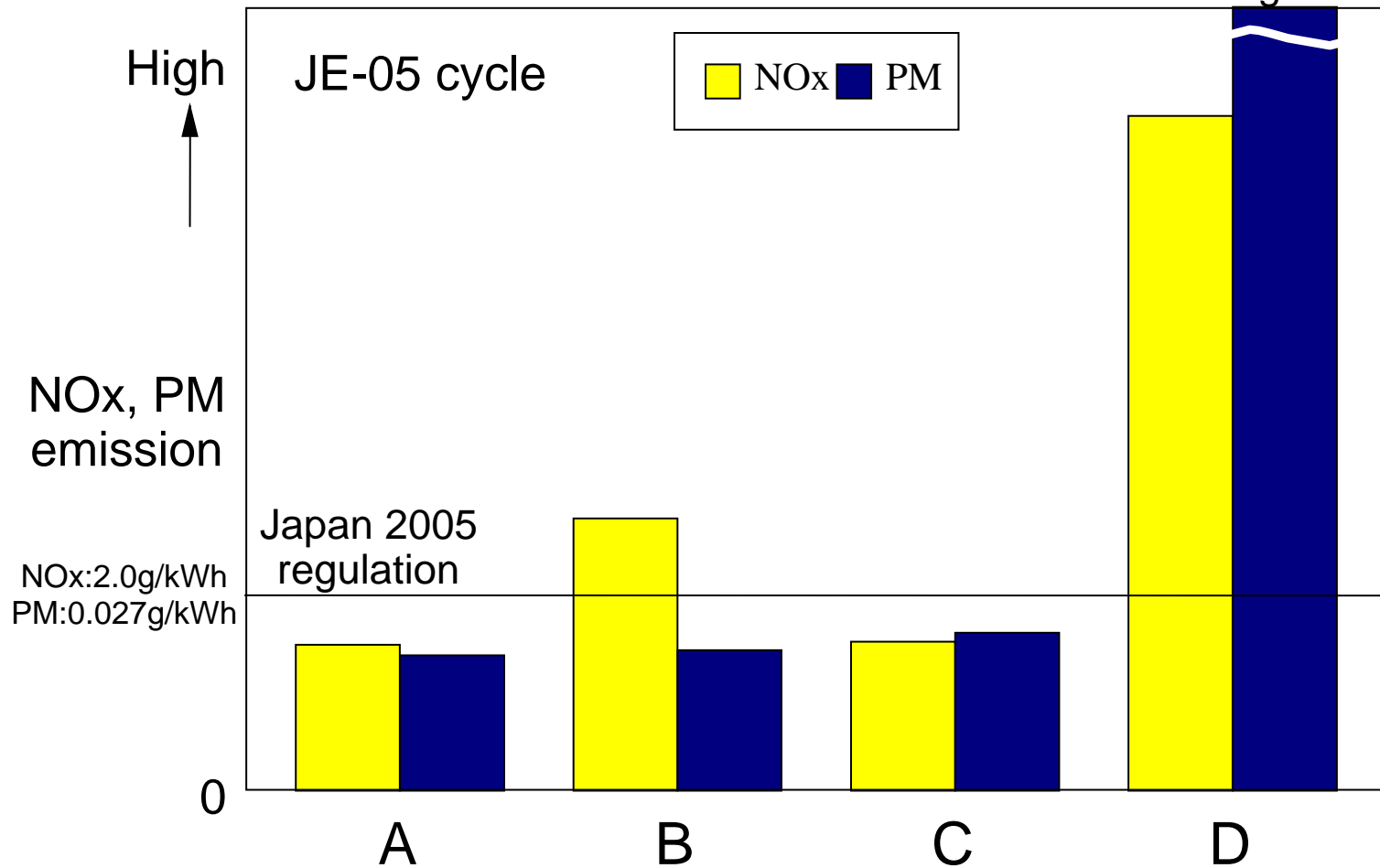
dummy: Catalyst without metal components
NH₃ was measured by only LDS

Emission test results (1)

Condition ID	DOC1	SCR	DOC2
A			
B		dummy	
C			dummy
D	dummy	dummy	dummy

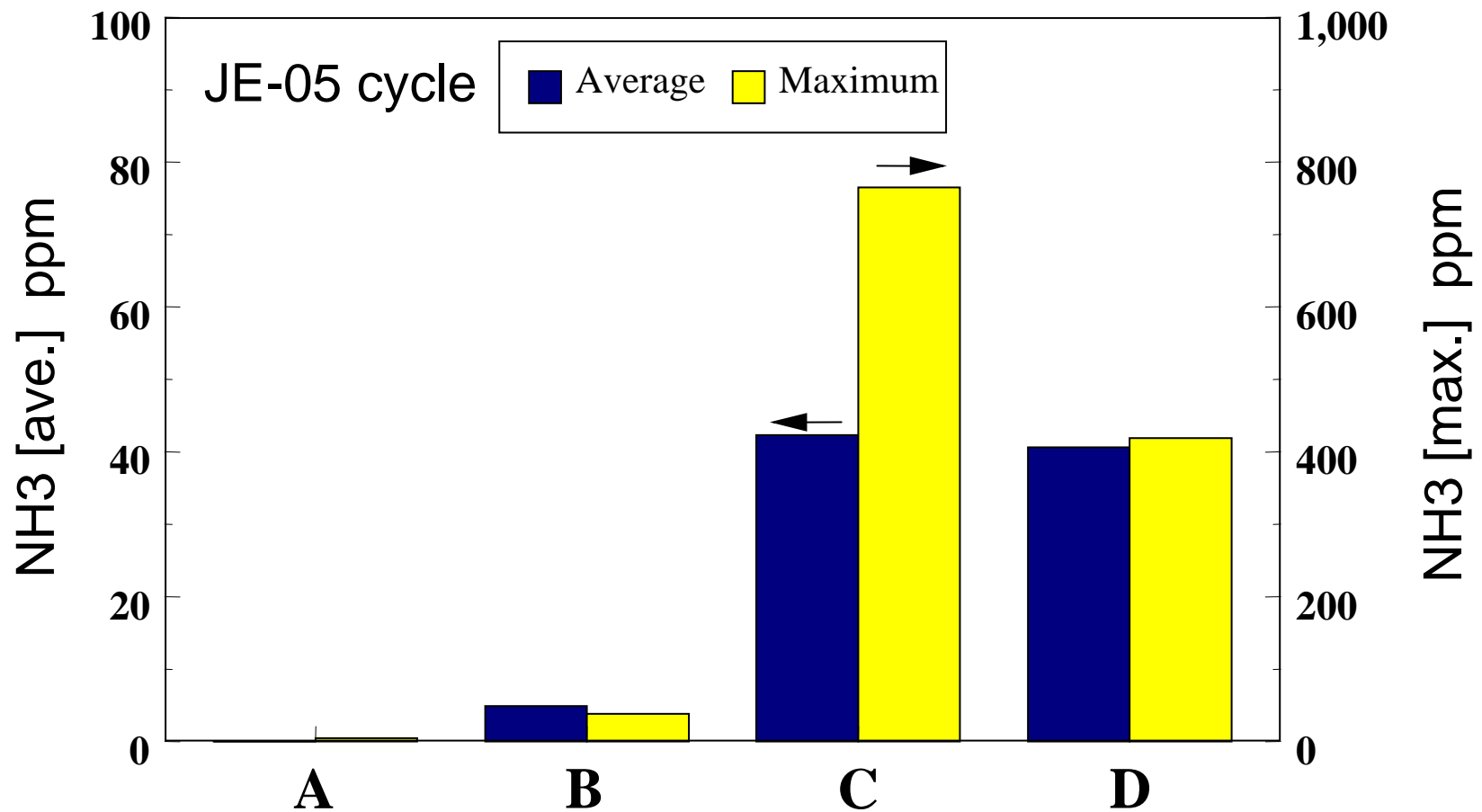
solid urea 98%

2.29g/kWh!



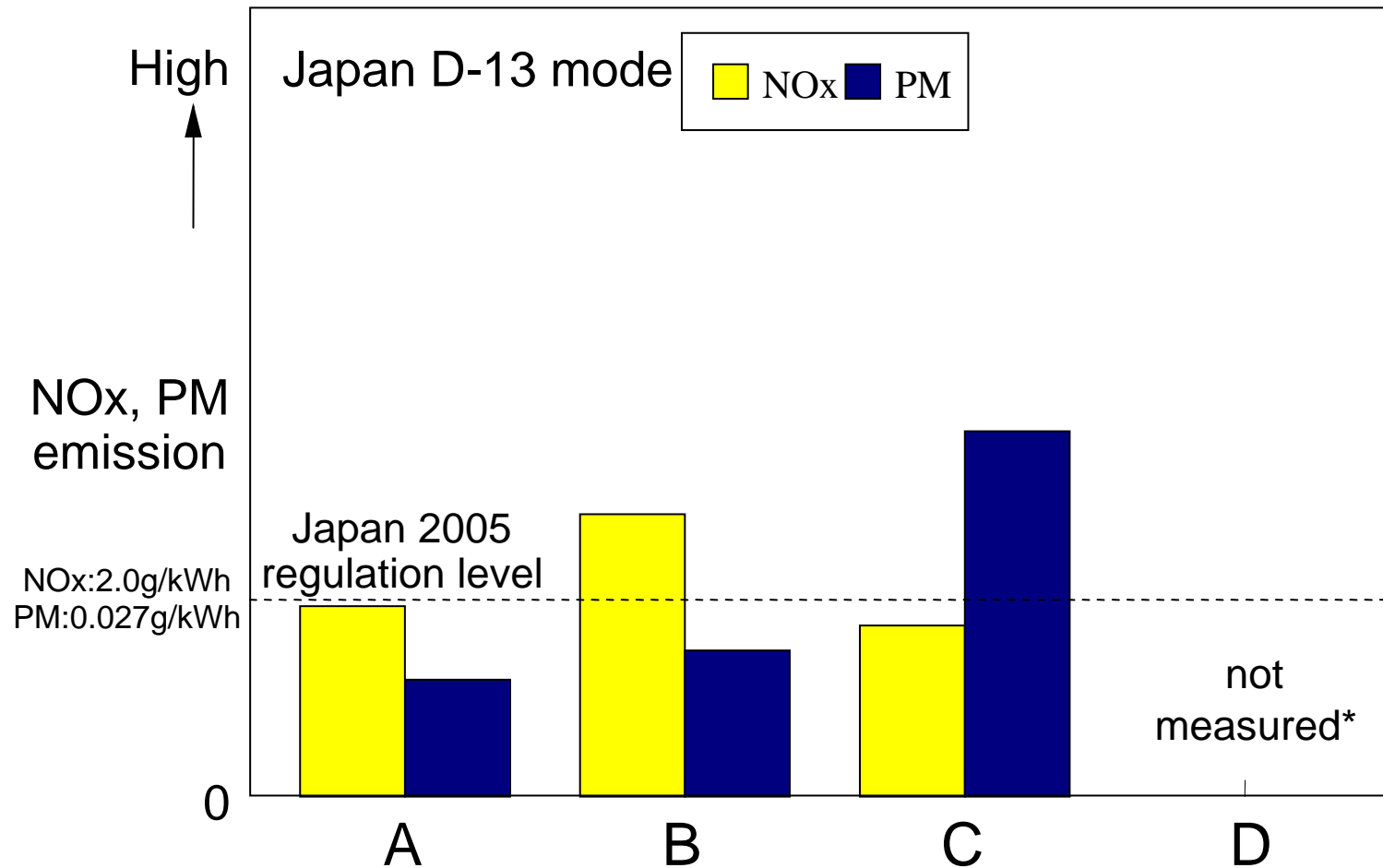
Emission test results (2)

Condition ID	DOC1	SCR	DOC2
A			
B		dummy	
C			dummy
D	dummy	dummy	dummy



Emission test results (3)

Condition ID	DOC1	SCR	DOC2
A			
B		dummy	
C			dummy
D	dummy	dummy	dummy



Presentation overview

- 1. Background (Emission regulation)**
- 2. Feasibility study of SCR vehicles**
- 3. Ammonia measurement test**
- 4. Activated and de-activated catalyst test**
- 5. Conclusion**

Conclusion (1)

- NH₃ from vehicle with urea SCR system real time measurement was conducted using four types of exhaust gas analyzer
- NH₃ emission level was low, so it was difficult to evaluate absolute accuracy.
- Characteristics of each measurement system were clarified
- Overview of comparison is as follows.

	DCLD	MS	FTIR	LDS
Accuracy	~			
Response			×	
Price		×		
Peak during transient mode	×		×	
Average concentration	~	~		
Total amount of emission	~	~		

Conclusion (2)

- When one of catalyst in urea SCR system stop function, not only NO_x and NH₃ but also PM may increase
- Most of PM is solid urea, when PM substantially increase in above case.
- If SCR catalyst is in deactivated condition, post oxidation catalyst (ammonia slip catalyst) can prevent NO_x, PM, and NH₃ from substantial increase.