

# ***Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation: Low-Temperature Storage Catalyst Test Protocol***

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## **SUMMARY**

Catalyst testing protocols are being developed to address the need for consistent and realistic metrics for aftertreatment catalyst evaluation. Catalyst testing protocols will consist of a set of standardized requirements and test procedures that sufficiently capture catalyst technology's performance capability and are adaptable in various laboratories. This document details a low temperature passive storage (and release) catalyst testing protocol.

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## BACKGROUND

Catalyst based vehicle aftertreatment development and characterization efforts are becoming multi-organizational partnerships exploiting the wide breadths of expertise from the various partners involved. These multi-partnership efforts have highlighted the need for standardized testing and characterization efforts to increase the consistency of data reporting. This initiative would also address a U.S. DOE and USDRIVE effort to improve evaluation and management of solicited projects. Therefore, to satisfy both requirements, the development of a series of standardized aftertreatment test protocols has been undertaken by the ACEC group of USDRIVE.

Catalytic aftertreatment can include single functionalities such as oxidation, reduction, adsorption, desorption, and physical filtration. However, current and future aftertreatment strategies often integrate multiple functionalities. “Device” is the term used to describe an aftertreatment system and strategy that may employ one or multiple functionalities. With this in mind, test protocols will likely take unique forms depending on multiple factors, including (i) the research activity the protocol is supporting, (ii) the nature and complexity of the aftertreatment strategy (e.g. conversion versus passive adsorption, singular versus multi-functionality), and (iii) the combustion platform of interest (e.g. diesel vs. gasoline, lean burn vs. stoichiometric combustion).

Research activities can be broadly characterized as performance screening, reaction engineering, or development to achieve a performance target. Performance-based protocols for screening catalyst reactions are global in nature, providing only the overall conversion efficiency of the species of interest; they must be simple to execute in a timely manner, as it is desirable to maximize the pace of catalyst development. This is in contrast to more detailed protocols intended to probe individual reaction steps of a global process (e.g., for supporting reaction engineering of predictive simulation efforts). In these instances, the focus is placed on isolating and characterizing each contributing reaction that supports the overall reaction scheme. This dictates that these protocols will be more complex and will likely place additional demands on the testing requirements needed.

The relative complexity of the aftertreatment process being studied is expected to affect the form of the protocol employed. The level of detail is primarily determined by the focus of the protocol being either a singular functionality or overall system performance characterization. In some cases, functionality and device performance are synonymous. Oxidation catalysis is a representative example of this case and is more straight-forward to probe. However, in many instances, multiple functionalities dictate overall device performance. An example of this is the oxidation catalyst with added zeolite to promote HC storage at low temperatures. In this instance, test protocols for such a system would require additional steps to adequately characterize performance. Therefore, the method of characterization will often differ as a function of the relative complexity required to adequately quantify performance. With respect to test procedures under consideration here, conversion-based processes are typically characterized by quantifying a single reaction or class of reactions, whereas adsorption-based processes are more complex and require the characterization of both capacity and response time (i.e. adsorption and desorption rates). Adsorption-based functionalities, therefore, are inherently more difficult to characterize and require more complex strategies.

The first test protocol, the *Low-Temperature Oxidation Catalyst Test Protocol*, has been completed and released to the technical community at <https://cleers.org/low-temperature-protocols/>. This document presents the second test protocol, which is focused on characterizing low temperature storage catalysts.

## OVERVIEW

This protocol is developed as a guide for conducting flow reactor studies for evaluating and comparing performance of aftertreatment catalyst technologies. The goal is to efficiently characterize the storage and release properties of candidate storage catalysts. Specifically, this protocol will address performance evaluation applicable to low temperature aftertreatment systems intended for advanced combustion strategies. Description of the protocol provided below is separated into five (5) sections: (i) reactor description and best practices, (ii) exhaust simulation, (iii) protocol execution, (iv) de-greening and aging, and (v) reporting.

The protocol is intended for application to both low temperature NO<sub>x</sub> storage (i.e., passive NO<sub>x</sub> adsorbers or PNAs) and low temperature hydrocarbon (HC) storage (i.e., HC traps). In the protocol, NO<sub>x</sub> is represented solely as NO since the form of NO<sub>x</sub> emitted from the engine is predominantly NO. HC is simulated as a combination of products of incomplete combustion and unburned fuel-type species, favoring the latter for low temperature application. This is accomplished by representing HC exhaust species with a small alkene (ethylene), an aromatic (toluene), and n-dodecane for diesel or ethanol + isooctane for gasoline, respectively.

The protocol is intended to assess the trapping and release properties of candidate storage and release catalysts. However, storage and release catalysts are not aftertreatment solutions, they provide a trapping functionality that is effective only when release is coupled (intimately or subsequently) with conversion. In reality, HC traps must be integrated with oxidation catalysis to function properly, and thus conversion must be considered in their evaluation. Similarly, passive NO<sub>x</sub> adsorbers (PNA) will have subsequent NO<sub>x</sub> reduction, which should be considered in testing. Conversion is included as a tool to assist in the assessment of the efficacy of storage & release materials towards a total aftertreatment solution, as considering solely storage & release may give misleading results. To capture both storage & release properties and conversion performance, it is suggested that the user conduct the protocol in duplicate:

1. With the trap material only to assess the storage and release properties of the developmental material
2. With the trap material and conversion catalyst (integrated appropriate to the application) to assess the device-level solution, and the relation of release properties to conversion.

## REACTOR DESCRIPTION AND BEST PRACTICES

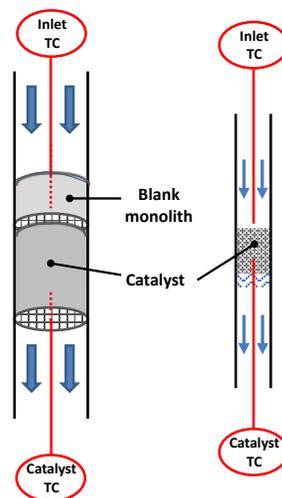
A reactor description is provided as a set of minimum configuration, instrumentation, sample, and reactor performance requirements for execution of the protocol. Design best practices, derived from industry, university, and national laboratory reactor experience, are provided as a guide to achieve accurate and reproducible results that can be easily shared throughout the aftertreatment R&D community.

### Configuration Requirements

Accurately characterizing storage necessitates the ability to switch between (1) a full reactor bypass with the simulated exhaust stream, and (2) flowing through the catalyst, due to the non-steady state nature of passive storage characterization. This differs from steady state conversion where slip-streams can be pulled for inlet and outlet characterization. The purpose of a full reactor bypass is to stabilize and characterize the feed concentrations prior to characterizing storage properties for the catalyst.

### Instrumentation Requirements

A minimum of two (2) thermocouples should be employed in the reactor configuration: (i) an inlet thermocouple intended to measure the temperature of the simulated exhaust stream entering the catalyst, and (ii) a catalyst thermocouple intended to measure the temperature of exhaust within the catalyst sample. The inlet thermocouple should be located less than ½-inch upstream of the catalyst bed (or the upstream-face of the core) but not in contact with the catalyst. The catalyst thermocouple should be embedded within the powder catalyst sample, preferably at or downstream axially of mid-bed and radially close to centerline from the exit face of the catalyst. In a monolithic core sample, the catalyst thermocouple should be inserted into a monolith channel near the radial centerline. A suggested maximum thermocouple diameter is 0.032 inch (~0.8 mm) to minimize adverse effects of the thermocouple on catalyst powder flow dynamics, or to avoid monolith damage as a result of thermocouple insertion. For core testing, it is best practice to place an inert monolith core just upstream of the catalyst, with the inlet thermocouple embedded within the inert core. This serves multiple functions: (i) it minimizes potential radiative heat effects from the furnace or heater and thereby provides a higher confidence in accuracy of the inlet temperature measurement, (ii) it insures the inlet thermocouple is located radially close to centerline and not in contact with the reactor wall, and (iii) it helps provide uniform flow distribution at the front face of the catalyst core sample.



**Figure 1 – Inlet and catalyst thermocouple (TC) placement**

Chemical analysis capability should include, at a minimum, quantitative analysis of the component being stored, and primary potential byproducts of the stored component. Thus, if NO is being stored, chemical analysis should include NO, NO<sub>2</sub>, and N<sub>2</sub>O; and NH<sub>3</sub> should be included for stoichiometric/rich testing. Similarly, if HC storage is being studied, chemical analysis should include, at a minimum, HC, CO, and CO<sub>2</sub>. Chemical analysis of each HC species in the feed stream is preferred, along with potential HC byproducts such as formaldehyde, acetaldehyde, and methane. If a total HC analysis technique is used and individual HC analysis is not feasible, the full HC blend should still be employed. Analytical capability less than the minimum recommended here will limit the usefulness and applicability of the results. The level of reproducible detection must be equal or greater to the relative conversion reported; e.g., reporting of 95% conversion of a component at 100 ppm feed dictates that reproducible detection of 5ppm is feasible for that component. The preferable resolution of an emission measurement is ≤2% of feed concentration, and capability less than this may limit the usefulness and applicability of results.

For adequately characterizing storage and release properties of catalysts, the frequency of sample analysis and the rate of response are very important. The frequency of sample analysis will dictate the relative fidelity of the data used to determine storage kinetics and the stored and released amounts. Therefore, a 1-Hz sample frequency is preferred. The rate of analysis response will control the ability to accurately characterize storage and release properties during testing, and specifically it will allow accurate identification of release temperatures. This can be characterized by the rate of response to a step-change in feed composition: a response time of  $\leq 15$  seconds is required to reach  $\geq 90\%$  of steady-state concentration following a step-change in feed composition. Together, these requirements exclude chromatography-based analytical techniques, and necessitate a 'real-time' analysis strategy (e.g., FT-IR, mass spectroscopy,  $\text{NO}_x$  chemiluminescence).

### Catalyst Sample Requirements

#### *Powder*

- Bed diameter (i.e. reactor ID)  $> 3$  mm and  $< 13$  mm
- Catalyst particle size should not exceed 600 micron (30 mesh), but it should be smaller if necessary to ensure adequate sample packing dependent upon reactor diameter
- If necessary, samples can be pressed into discs and broken into larger particles of desired sizes
- Catalyst bed aspect ratio (length/diameter)  $\geq 1$

#### *Monolith Core*

- Core diameter  $> 12$  mm, preferably  $> 19$  mm
- A well-defined conventional core substrate (e.g., cordierite, SiC, Al-titanate, etc.)
- 400 CPSI preferred, or as appropriate to the application
- Catalyst bed aspect ratio (length/diameter)  $\geq 1$

### Reactor Performance Requirements

For protocol testing, it is best practice to minimize any thermal gradients within the catalyst sample. Therefore, in nitrogen-only flow the allowable temperature gradient measured between the inlet thermocouple and catalyst thermocouple is  $\leq 5^\circ\text{C}$  at  $100^\circ\text{C}$  feed and  $\leq 20^\circ\text{C}$  at  $500^\circ\text{C}$  feed. If a dedicated pre-heating furnace is employed (in addition to a catalyst furnace), this can generally be accomplished. However if only a single catalyst furnace is employed, it is best practice to place the catalyst close to the outlet of the actively heated zone.

Reactor "base-lining" is to be performed once per specific application and per unique apparatus configuration. It should be repeated following any significant hardware repair, replacement, or reconfiguration. Reactor base-lining is conducted by executing the full protocol with an empty reactor tube or inert sample. The recovery of reactants over the temperature ramp of the protocol should be  $\geq 95\%$ . Please note that at very high temperatures ( $>450^\circ\text{C}$ ) gas phase reactions may occur that can be ignored. Additionally, since storage and release measurements are transient in nature, it is also important to use reactor "base-lining" to characterize any equipment derived transients. Any equipment-derived transients can then be accounted for in the data analysis so that their presence does not misrepresent material performance.

### Additional Reactor Configuration and Operation Requirements and Recommendations

- System leak checked daily and following each sample change or any hardware re-configuration.
- Analyzer calibration at least once daily (e.g. zero gases and span gases).
- Inlet gas composition characterized and stabilized prior to each storage/release event.

- Passivated stainless steel tubing for gas transport to and from the reactor (recommended).
- All gas transport lines heated to appropriate temperature to prevent condensation; all reactor sampling lines heated to  $\geq 190^{\circ}\text{C}$  to prevent condensation or absorption.
- If employing dedicated pre-heating, it is suggested to pre-heat inert species only (e.g. air,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ). Care should be taken with regards to particularly difficult reactants, e.g. high boiling point (high MW) HC,  $\text{NH}_3/\text{NO}_2$ . These should be added to pre-heated exhaust as close to the catalyst as possible, while allowing for adequate mixing (recommended).
- Calibrate mass flow controllers at least once per year or according to manufacturer guidelines (recommended).

### EXHAUST SIMULATION

This protocol is intended to characterize the storage and release properties of catalysts proposed for a specific combustion mode and a targeted storage component by modifying the gas composition of the simulated exhaust. The protocol will consist of sequential pre-treatment, storage, and release events with potentially unique gas compositions employed during each event. The recommended gas compositions for the simulated engine-out exhaust are detailed in Table 1 for stoichiometric GDI (S-GDI, diluted with EGR), clean diesel combustion (CDC), lean gasoline direct injection (L-GDI), low temperature combustion of diesel (LTC-D), and low temperature combustion of gasoline (LTC-G). The difference between measured and targeted gas concentrations (from Table 1) should be  $\leq 10\%$ . If the user does not have a targeted application for their development efforts, it is suggested that they employ the CDC conditions as default.

**Table 1 – Simulated engine-out exhaust parameters for storage characterization <sup>(a)</sup>**

Constant components	S-GDI	CDC		L-GDI	LTC-G	LTC-D
[O <sub>2</sub> ]	0.74%	12%		9%	12%	12%
[H <sub>2</sub> O]	13%	6%		8%	6%	6%
[CO <sub>2</sub> ]	13%	6%		8%	6%	6%
Variable components	all in [ppm]					
[CO]	5000	500		2000	2000	2000
[H <sub>2</sub> ] <sup>(b)</sup>	1670	100		670	670	400
[NO]	1000	200		500	100	100
	Hydrocarbon – [ppm] on C <sub>1</sub> basis					
Total [HC]	3000	1400		3000	3000	3000
[C <sub>2</sub> H <sub>4</sub> ]	900	400		400	400	900
[C <sub>2</sub> H <sub>5</sub> OH]	110			110	110	
[C <sub>7</sub> H <sub>8</sub> ]	900	300		1400	1400	900
[i-C <sub>8</sub> H <sub>18</sub> ]	1090	-		1090	1090	-
[n-C <sub>12</sub> H <sub>26</sub> ]	-	700		-	-	1200

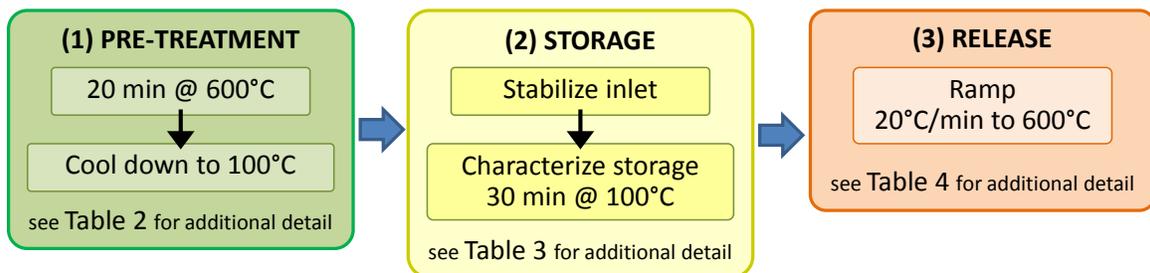
<sup>(a)</sup> Balance N<sub>2</sub>

<sup>(b)</sup> Held at constant percentage of [CO]

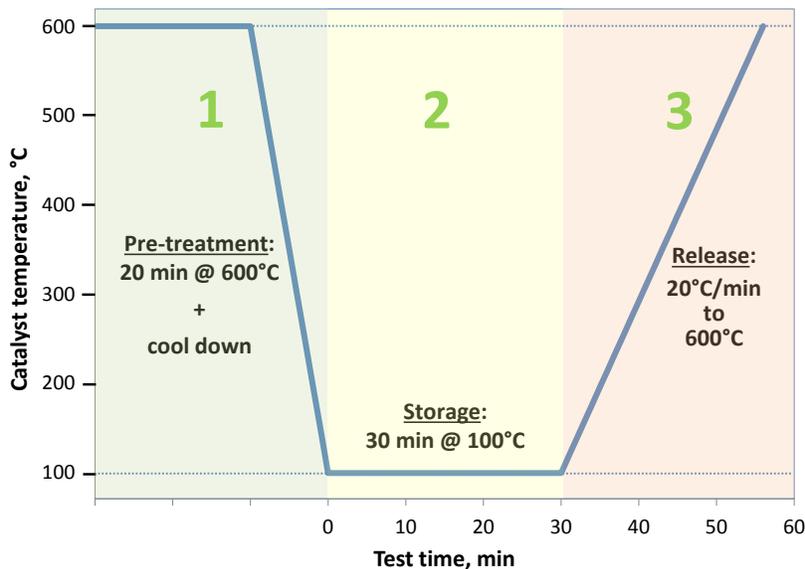
**PROTOCOL EXECUTION**

The protocol should only be executed on a catalyst that has been, at a minimum, fully calcined and de-greened. See **DE-GREENING AND AGING** for more information. As shown in Figures 2 and 3, protocol execution consists of three (3) separate events conducted in sequential fashion as follows:

- (1) Initial pre-treatment to ensure that common conditions prevail for accurate comparative catalyst assessment, and then cool down.
- (2) Storage characterization isothermally at 100°C for 30 minutes.
- (3) Release (& conversion) characterization consisting of a fast thermal ramp (20°C/min) to 600°C.



**Figure 2 – Storage protocol test strategy**



**Figure 3 – Storage protocol temperature control**

Pre-treatment

Table 2 provides detail for the pre-treatment step of the protocol. Pre-treatment, which is to be conducted before each storage/release test event, consists of heating the catalyst to 600°C and holding for 20 minutes, followed by cooling back down to the storage temperature. Pre-treatment is performed lean for all combustion modes to oxidize any material on the catalyst and to ensure that common conditions prevail prior to the characterization of storage. The user should use the concentrations of O<sub>2</sub>,

H<sub>2</sub>O, CO<sub>2</sub> (balance N<sub>2</sub>) found in Table 1 for the intended combustion mode for the application. If the user is unsure of the intended application, it is suggested that they employ the CDC conditions as default.

Following lean pre-treatment, the metal on the catalyst will likely be in an oxidized state. This is appropriate for lean combustion modes, but it is not representative of catalysts used on stoichiometric applications (i.e., S-GDI). Thus, when considering metal-catalyzed reactivity, this may not accurately reflect a catalyst's activity (or lack thereof) for S-GDI emission reduction (e.g., oxidation, or HC-SCR). For that reason, pre-treatment for S-GDI applications includes a hold point at 350°C under rich conditions following the 600°C lean pre-treatment and prior to cooling to the storage temperature to ensure a realistic oxidation state of metal on the catalyst.

Following cooling of the catalyst to the 100°C storage temperature, a 5 minute (minimum) hold period is included. This hold period at the storage temperature is important for ensuring that the catalyst bed is radially and axially isothermal prior to flow bypass for inlet stabilization and subsequent storage characterization.

### Storage

The default storage temperature is 100°C. To investigate various storage temperatures, the protocol should be re-run in its entirety at the different storage temperatures. Table 3 provides detail for the storage step of the protocol. It is expected that in application, the storage event will occur under conditions at which the catalyst is exposed to the full engine-out exhaust. For that reason, storage characterization employs the full simulated exhaust for the desired application given in Table 1. It consists of stabilizing the inlet to the reactor under a full-reactor bypass, followed by switching flow through the reactor & catalyst and characterizing storage isothermally for 30 minutes.

### Release (or Release + Conversion)

Release (or release & conversion) is characterized immediately following storage per the detail provided in Table 4. This consists of a 20°C/min thermal ramp from the storage temperature (100°C) to 600°C. The exhaust composition for the release (or release & conversion) step is dictated by the conditions at which release is expected to occur. For lean combustion modes, the HC and NO<sub>x</sub> release events are expected to occur at temperatures above oxidation catalyst light-off for oxidation of CO, H<sub>2</sub>, and most HC species. In addition, NO<sub>x</sub> reduction is expected to occur subsequent to (i.e., downstream from) any HC or NO<sub>x</sub> storage functionality. For this reason, the HC and NO<sub>x</sub> release steps for lean combustion modes are conducted without HC/CO/H<sub>2</sub> in the feed but in the presence of NO<sub>x</sub>. For stoichiometric combustion modes (i.e., S-GDI), release is expected to occur at temperatures above TWC light-off. For this reason, HC release for S-GDI applications is conducted without HC/CO/H<sub>2</sub> or NO<sub>x</sub> in the feed. For the various combustion modes, this is summarized as follows:

- NO<sub>x</sub> release (and release & conversion) characterization is performed in the presence of O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and NO<sub>x</sub> (balance N<sub>2</sub>) for all combustion modes.
- HC release (and release & conversion) characterization is performed in the presence of O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and NO<sub>x</sub> (balance N<sub>2</sub>) for all combustion modes *besides* S-GDI.
- HC release (and release & conversion) characterization for S-GDI is performed in the presence of O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> (balance N<sub>2</sub>).

**IMPORTANT** – The magnitude of the thermal ramp employed during the release (or release + conversion) has a potentially significant effect on the release properties of the catalyst. For this reason, it is imperative that consistent thermal ramping be employed for accurate comparative evaluation of catalyst performance from test to test.

During release, the presence of CO<sub>2</sub> in the feed makes it difficult to accurately quantify the extent of conversion (HC oxidation or HC-SCR of NO<sub>x</sub>), with the only strategy being to compare the total

amount released to the total amount stored. For a more accurate assessment of total conversion, users may wish to omit CO<sub>2</sub> from the feed stream to allow CO<sub>2</sub> analysis out of the catalyst as a direct measure of HC conversion. See Appendix C for more details.

**Table 2 – Step 1 of protocol: Pre-treatment**

<b>PRE-TREATMENT – CDC, LTC-D, LTC-G, L-GDI</b>									
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							Bypass
LTP-2-1P	Pretreat 20 min @ 600°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
LTP-2-2P	Cool 600°C to 100°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
LTP-2-3P	Hold 5 min @ 100°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
<b>PRE-TREATMENT – S-GDI</b>									
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							Bypass
LTP-2-1PS	Pretreat 20 min @ 600°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
LTP-2-2PS	Cool 600°C to 350°C	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
LTP-2-3PS	Reduce 5 min @ 350°C	-	3% CO	1% H <sub>2</sub>	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
LTP-2-4PS	Cool 350°C to 100°C	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off
LTP-2-5PS	Hold 5 min @ 100°C	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	Off

<sup>(a)</sup> Bracketed concentration values are combustion-mode dependent and found in Table 1

**Table 3 – Step 2 of protocol: Storage**

<b>STORAGE – all modes</b>										
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							Time	Bypass
LTP-2-3S	Hold 100°C	[HC]	[CO]	[H <sub>2</sub> ]	[NO]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-( <sup>b</sup> )	On
LTP-2-4S	Hold 100°C for 30 min	[HC]	[CO]	[H <sub>2</sub> ]	[NO]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	30 min	Off

<sup>(a)</sup> Bracketed concentration values are combustion-mode dependent and found in Table 1

<sup>(b)</sup> For inlet characterization; dependent on time required to stabilize inlet concentrations

**Table 4 – Step 3 of protocol: Release (or Release & Conversion)**

<b>NOx RELEASE – all modes</b>										
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							Time	Bypass
LTP-2-5RN	Ramp 20°C/min to 600°C	-	-	-	[NO]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	26 min	Off
<b>HC RELEASE – CDC, LTC-D, LTC-G, L-GDI</b>										
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							Time	Bypass
LTP-2-5RH	Ramp 20°C/min to 600°C	-	-	-	[NO]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	26 min	Off
<b>HC RELEASE – S-GDI</b>										
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							Time	Bypass
LTP-2-5RHS	Ramp 20°C/min to 600°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	26 min	Off

<sup>(a)</sup> Bracketed concentration values are combustion-mode dependent and found in Table 1

**DE-GREENING AND AGING**

The protocol should only be executed on a catalyst that has been, at a minimum, fully de-greened to insure a common and stabilized initial state of performance. De-greening is not intended to replace full and complete catalyst calcination; calcination should occur as part of catalyst synthesis, and all catalysts should be fully calcined prior to de-greening. Procedures for catalyst de-greening are described in this section. Catalyst de-greening is not included as part of the protocol test strategy, but should be done prior to activity characterization. It is important to note that the pre-treatment portion of the protocol is not intended to replace adequate de-greening.

The catalyst aged state is considered a constant parameter in the protocol. Procedures for providing a realistic and representative aged state are described in this section. If it is the user’s intent to characterize activity of an aged catalyst, then the procedures for catalyst aging should be completed prior to the test protocol. Catalyst aging consists of both thermal aging and chemical poisoning. It is suggested that the user first characterize activity of the de-greened catalyst, followed by thermal aging and chemical poisoning in sequential fashion, with the test protocol conducted following each treatment.

Please note that catalysts for use in low temperature combustion of gasoline (LTC-G) applications are de-greened and aged analogous to gasoline GDI SI combustion strategies, as it is currently expected that LTC-G combustion strategies will require SI combustion strategies under certain conditions. This dictates that de-greening and aging must defer to SI conditions (LTP-1DG-G and LTP-1A-G-1 to -3, respectively). If the user’s application intends to employ LTC-G combustion strategies over the entire engine cycle, then de-greening and aging can defer to lean combustion conditions (LTP-1DG-D and LTP-1A-D-1, respectively). However, this will limit the usefulness and applicability of results to solely that condition.

Catalyst De-greening

The de-greening conditions are shown in Table 5, and consist of neutral conditions (10% CO<sub>2</sub>, 10% H<sub>2</sub>O, balance N<sub>2</sub>) for all gasoline applications (S-GDI, L-GDI, LTC-G), and lean conditions (10% O<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>) for all diesel applications (CDC, LTC-D). The de-greening procedure consists of exposing the catalyst to the most applicable mixture for the application (referencing Table 1), ramping from room temperature to 700°C and holding for 4 hours. The user should perform only a single de-greening per catalyst sample. The temperatures noted for catalyst de-greening refer to the catalyst inlet temperature.

**Table 5 – Catalyst de-greening parameters**

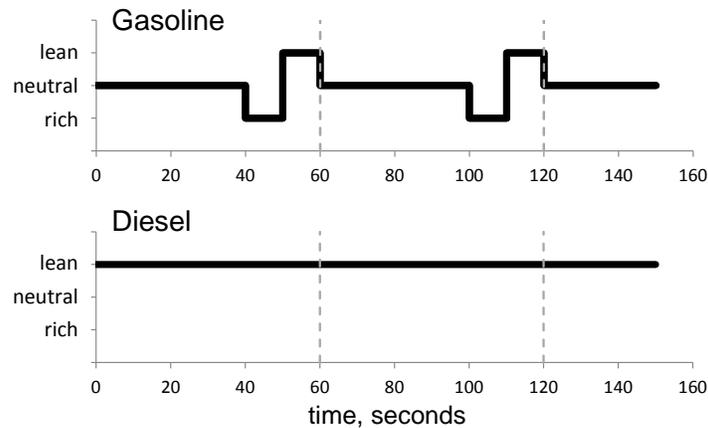
<b>S-GDI, L-GDI, LTC-G</b>					
Step No.	Mode	Condition	Exhaust make-up (balance N <sub>2</sub> )		
			[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]
LTP-1DG-G	Neutral	700°C/4 hours	-	10%	10%
<b>CDC, LTC-D</b>					
Step No.	Mode	Condition	Exhaust make-up (balance N <sub>2</sub> )		
			[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]
LTP-1DG-D	Lean	700°C/4 hours	10%	5%	5%

**Catalyst Thermal Aging**

Thermal aging representative of anticipated in-use durability requirements is to consist of 50 hours continuous operation at 800°C inlet temperature, with the gas composition dependent on the combustion mode which the aftertreatment technology will address. As detailed in Table 6 and Figure 4, gasoline applications will employ a 1-minute cycle consisting of 40 seconds neutral, 10 seconds rich, and 10 seconds lean operation conducted in continuous sequential fashion for the 50 hours at 800°C. Diesel applications will employ continuous lean operation over the entire 50 hours. Users should conduct only a single 50-hour aging cycle per catalyst. As with de-greening, the temperatures noted above for thermal aging refer to the catalyst inlet temperature.

**Table 6 – Catalyst aging cycle parameters**

S-GDI, L-GDI, LTC-G							
Step No.	Cycle mode	Duration	Exhaust make-up (balance N <sub>2</sub> )				
			[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]	[CO]	[H <sub>2</sub> ]
LTP-1A-G-1	Neutral	40 seconds	-	10%	10%	-	-
LTP-1A-G-2	Rich	10 seconds	-	10%	10%	3%	1%
LTP-1A-G-3	Lean	10 seconds	5%	10%	10%	-	-
CDC, LTC-D							
Step No.	Cycle mode	Duration	Exhaust make-up (balance N <sub>2</sub> )				
			[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]	[CO]	[H <sub>2</sub> ]
LTP-1A-D-1	Lean	Continuous	10%	5%	5%	-	-

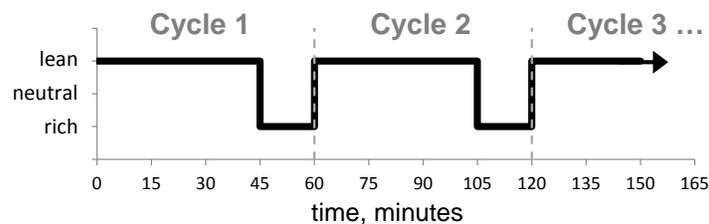


**Figure 4 – Catalyst aging cycles**

For diesel applications, the presence of an LNT will require periodic rich operation for desulfurization. This is particularly stressful for aftertreatment catalysts and must be addressed separately for aging. To be considered for deployment together with an LNT, the catalyst must be thermally aged an additional 10 hours at 800°C as described in Table 7 and Figure 5; this is in addition to the 50-hour thermal aging cycle for all diesel applications from Table 6 (LTP-1A-D-1). The LNT aging is a 1-hour cycle consisting of 45 minutes lean and 15 minutes rich operation conducted 10 times in continuous sequential fashion for a total of 10 hours at 800°C. For diesel LNT applications, the user should characterize catalyst performance following the initial 50-hour lean thermal aging cycle, and then a second time following the 10-hour LNT thermal aging cycle.

**Table 7 – Diesel with LNT catalyst aging cycle parameters**

CDC, LTC-D							
Step No.	Cycle mode	Duration	Exhaust make-up (balance N <sub>2</sub> )				
		1-hour cycle	[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]	[CO]	[H <sub>2</sub> ]
LTP-1A-D-LNT-1	Lean	45 minutes	10%	5%	5%	-	-
LTP-1A-D-LNT-2	Rich	15 minutes	-	5%	5%	3%	1%

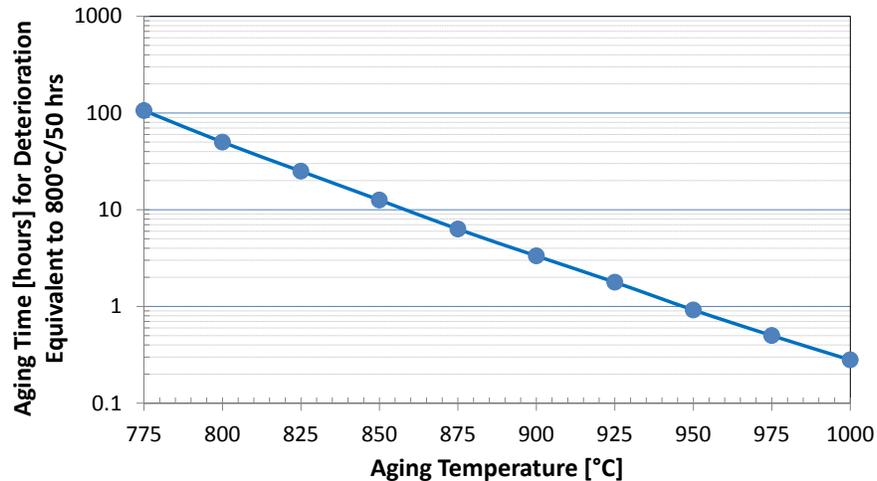


**Figure 5 – Diesel with LNT catalyst aging cycle**

Temperature Control during Thermal Aging

Physical and chemical changes of a catalyst due to thermal exposure are generally expected to follow an exponential increase with temperature described by an Arrhenius type relationship. As such, deviations in aging temperature between successive tests run for comparison or quality purposes can exhibit different results if the temperature is not controlled adequately. An example of the relationship between equivalent aging hours and temperature is shown in Figure 6. Thus, accurate and repeatable temperature and methodology control during catalyst aging procedures is important, especially when sequential tests will be used to compare different catalyst formulations or designs. It is recommended that temperature control for catalyst aging be held to +/- 2°C of the desired temperature. Additionally, it is emphasized the importance of controlling catalyst inlet temperature rather than bed temperature, since the former is more conducive to stable and repeatable operation.

**Aging Hours as a Function of Aging Temperature to Provide Equivalent Deterioration to 50 hrs at 800°C**



**Figure 6 – Aging equivalent hours with temperature differing from 800°C set point**

Chemical Poisoning

Chemical poisoning will initially focus only on transitory poisons in the form of sulfur derived from in-use fuels. A total exposure level of approximately 1 g sulfur per liter of catalyst (for core samples) is to be achieved by exposing the catalyst to 5 ppm SO<sub>2</sub> added to the full simulated exhaust at 30,000 hr<sup>-1</sup> SV and 300°C catalyst inlet temperature for 5 hours. For powder samples, sulfur exposure is to be performed at 200 L/g-hr under the same conditions, resulting in approximately 7 mg sulfur exposure per gram of catalyst.

As shown in Table 8, poisoning is to occur following the applicable pre-treatment and prior to cooling to the storage temperature. For S-GDI, applicable pre-treatment includes both the 600°C hold as well as reduction of the metal on the catalyst at 300°C. Following sulfur exposure, SO<sub>2</sub> is to be removed from the feed and the sample cooled to 100°C at which point the rest of the protocol is to be executed. The pre-treatment and cooling steps are to be performed in the presence of O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> (balance N<sub>2</sub>) for CDC, LTC-D, LTC-G, and L-GDI. For S-GDI, the pre-treatment and cooling steps are to be performed in the presence of H<sub>2</sub>O and CO<sub>2</sub> only (balance N<sub>2</sub>).

**DESULFATION** – If the user demonstrates an attractive candidate catalyst that is adversely affected by sulfur exposure, then it is strongly suggested that the user conduct and report a successful desulfation procedure, including temperature, time, and conditions. This may necessitate a multi-step and/or multi-temperature investigation, potentially including lean, stoichiometric, and/or rich conditions and temperatures as high as ~750°C. Due to the potentially widely-varying conditions required for successful desulfation, additional detail is not provided in this document; pursuit of appropriate conditions is left to the user. In the absence of reporting of such conditions and results, a significantly adverse impact to sulfur will be viewed as prohibitively challenging and potentially result in marginal interest in the catalyst.

**Table 8 – Catalyst poisoning parameters**

CDC, LTC-D, LTC-G, L-GDI										
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>								Bypass
LTP-1P-1	Pretreat 20 min @ 600°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-	Off
LTP-1P-2	Cool 600°C – 300°C	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-	Off
LTP-1P-3	Poison 5 hrs @ 300°C	[NO]	[CO]	[H <sub>2</sub> ]	[HC]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	5ppm SO <sub>2</sub>	Off
LTP-1P-4	Cool 300°C – 100°C <sup>(b)</sup>	-	-	-	-	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-	Off
S-GDI										
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>								Bypass
LTP-1P-1S	Pretreat 20 min @ 600°C	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-	Off
LTP-1P-2S	Cool 600°C – 300°C	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-	Off
LTP-1P-3S	Reduce 5 min @ 300°C		3% CO	1% H <sub>2</sub>	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]		Off
LTP-1P-3S	Poison 5 hrs @ 300°C	[NO]	[CO]	[H <sub>2</sub> ]	[HC]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	5ppm SO <sub>2</sub>	Off
LTP-1P-4S	Cool 300°C – 100°C <sup>(b)</sup>	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-	Off

<sup>(a)</sup> Bracketed concentration values are combustion-mode dependent and found in Table 1

<sup>(b)</sup> 100°C or the targeted storage temperature for the given run

**REPORTING**

When reporting on catalyst performance, all applicable details of the catalyst sample, reactor configuration, and test conditions should be reported along with the catalyst performance data. Additionally, it is important to demonstrate and comment on the reproducibility of the data set.

Catalyst Sample

For monolith core samples, details that should accompany catalyst test results include:

- Core length and diameter
- Cell density, i.e., cells per square inch (CPSI)
- Substrate wall thickness
- Substrate composition, e.g., cordierite, aluminum titanate
- Washcoat loading density, e.g., grams/in<sup>3</sup>

For powder samples, details that should accompany catalyst test results include:

- Mass of the catalyst sample tested
- Catalyst bed dimensions, i.e., bed length and diameter
- If possible, catalyst particle size range, i.e., mesh-size

For all catalyst samples (monolith and powder), general information is required regarding the catalyst composition (e.g., PGM loading and make-up).

Reactor Configuration

A minimum level of reactor and test configuration detail should accompany catalyst test results. This includes:

- Reactor tube (e.g., catalyst housing) description and dimensions
- Catalyst heating method (e.g., furnace description and configuration, pre-heater description)
- Location and orientation of catalyst sample within the heating apparatus
- Thermocouple description and location

- Chemical analysis technique(s) and instrumentation used (e.g., MKS 2030 MultiGas FTIR)
- Pertinent chemical analysis sampling details, such as temperature of sampling lines and any sample conditioning performed
- Water vaporization hardware for adding water to the simulated exhaust
- Liquid hydrocarbon vaporization hardware and technique, if used, for inclusion of liquid hydrocarbons (i.e., iso-octane or dodecane) in the simulated exhaust

### Test Conditions

Full details of the conditions employed for testing catalyst performance should accompany the reported results, including, at a minimum, the items listed below.

- The intended engine application/combustion strategy
- The procedures used for de-greening and/or aging the catalyst(s) prior to activity characterization, including gas composition, flowrate, temperature, and hold times, if they are different than those specified in Tables 5 through 7. If they are not, then referencing the applicable table(s) and engine application (i.e., combustion strategy) is sufficient
- The procedures used for pre-treating or poisoning the catalyst(s) and measuring performance, including gas compositions, flowrate, pre-treatment and storage temperatures, hold times, and ramp rates, if they are different than those specified in Tables 1 through 4, and 7. Again, if they are not, then referencing the applicable tables and engine application is sufficient

### Test Results/Performance Data

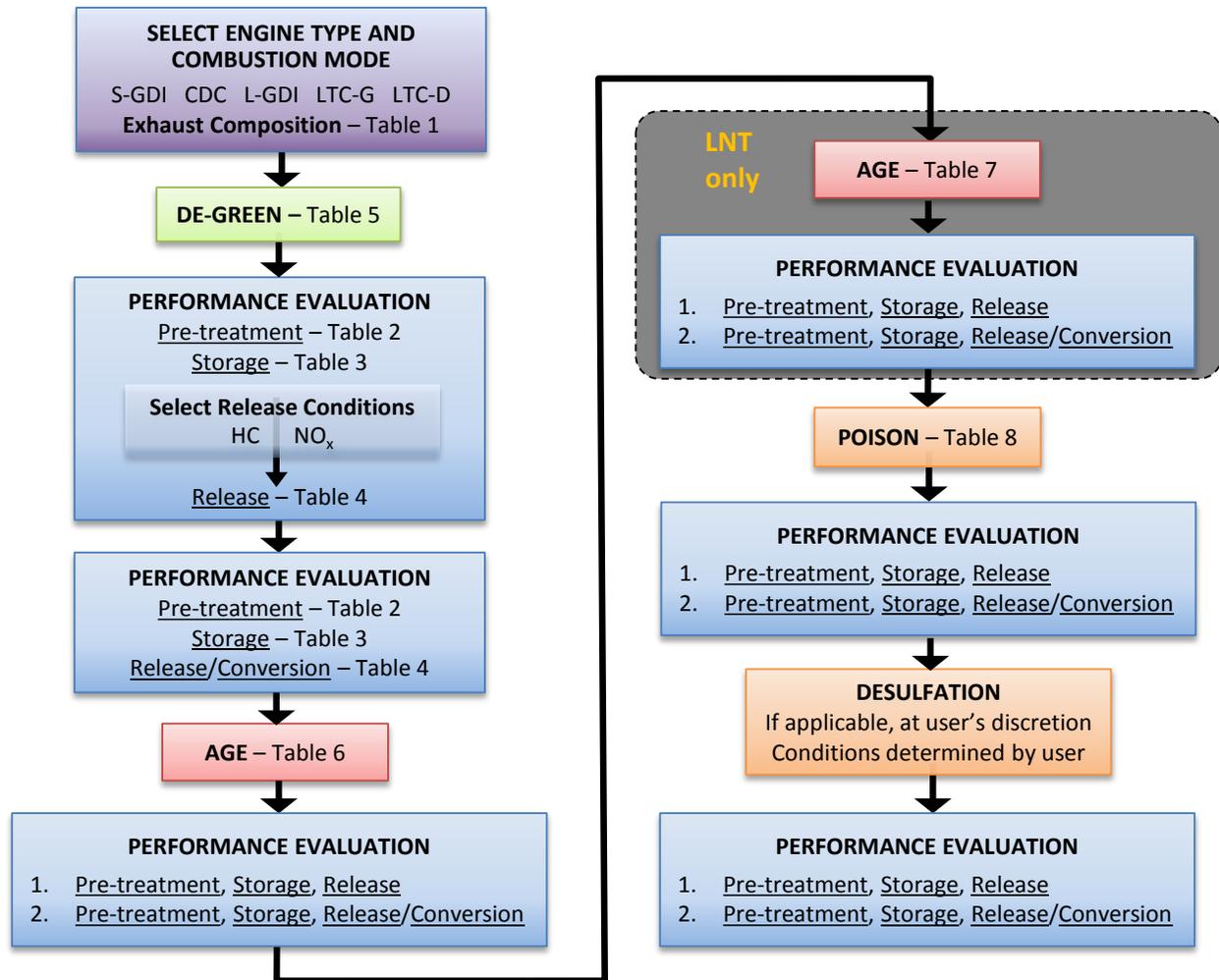
The catalyst performance data should include the following items for each test:

- Inlet component concentration(s) characterized prior to storage
- *Storage information*
  - Quantity of NO<sub>x</sub>/HC stored on the catalyst, i.e., the amount of NO<sub>x</sub>/HC removed from the inlet during the storage phase
    - Powders: gram of NO<sub>x</sub>/HC stored per gram of catalyst
    - Cores: gram of NO<sub>x</sub>/HC stored per liter of monolith
  - NO<sub>x</sub>/HC storage efficiency (fraction of NO<sub>x</sub>/HC in the inlet that is stored on the catalyst) for a given period of time
- *Release information*
  - Quantity of NO<sub>x</sub>/HC released during the release phase
    - ... or fractional recovery compared to the amount stored
  - Release temperature
    - Information relative to the relation of release and temperature.
    - This can be T10, T50 values, which are the temperatures of 10% & 50% release, respectively (90% & 50% is released above this temperature, respectively)
    - Or alternatively, it can be the fraction released at a given set of temperatures.
    - Percentages are relative to the total amount *released* from the catalyst, to account for conversion of a fraction of the stored component.
    - If CO<sub>2</sub> is being omitted for carbon balancing, see Appendix C for additional detail.
  - Byproduct formation

- *Release + Conversion information*
  - Desorbed NO<sub>x</sub>/HC conversion efficiency, i.e., the fraction of the quantity of NO<sub>x</sub>/HC released from the catalyst that is converted
  - Net emission benefit impact, i.e., storage efficiency multiplied by conversion efficiency
  - Byproduct formation
- *Desulfation*
  - If necessary, a desulfation procedure and subsequent performance results.
- It is also suggested that the user provide traces of component concentrations and temperature versus time for the storage and release portions of the tests.
  - This provides information associated with the kinetics of the storage and release properties of the catalyst.

**APPENDIX A: PROTOCOL FLOW CHART**

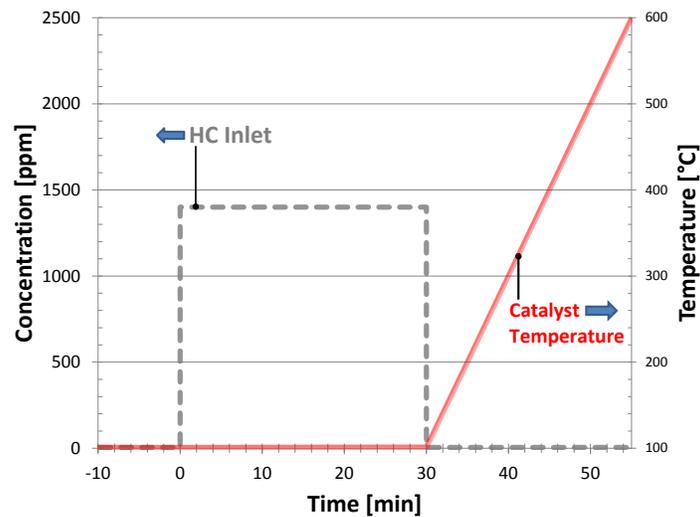
It is suggested that the user conduct catalyst testing in the order as it appears in Figure A1 below. An appropriate set of testing conditions should be selected based on the engine type (diesel vs. gasoline), combustion mode (CDC vs. LTC-D, or LTC-G vs. L-GDI vs. S-GDI), and application (HC versus NO<sub>x</sub> storage) that the catalyst is expected to support. If multiple engine types are to be investigated, this should be done with separate samples. If the user wishes to test aged catalysts only, then aging can be conducted without requiring an initial de-greening.



**Figure A1 – Test strategy flow chart for storage catalyst test protocol**

**APPENDIX B: PERFORMANCE DATA**

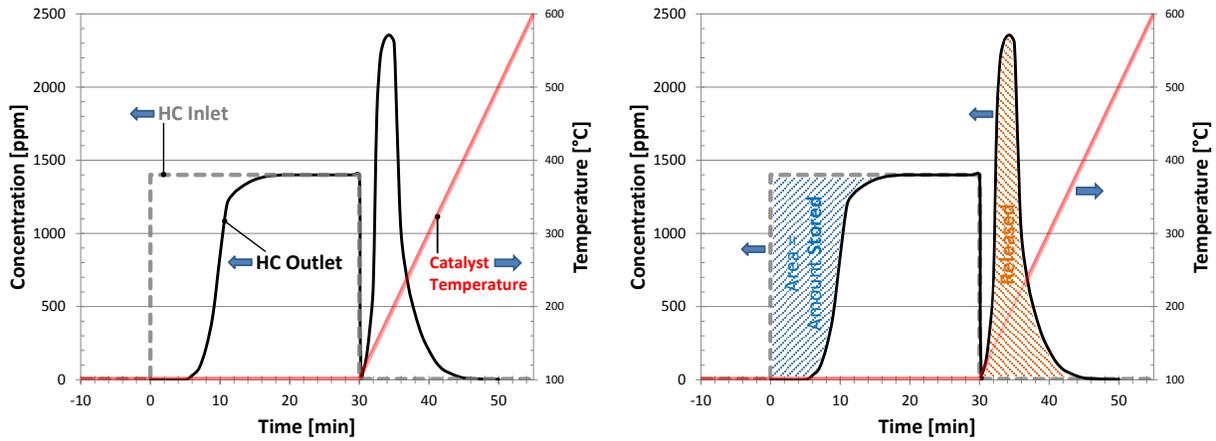
As a transient process, accurately reporting catalyst performance begins by graphically representing the data (both storage and release) as a function of time. This should start with reporting the way in which the test was performed, with Figure B1 shown for illustrative purposes. In Figure B1, the test begins when the stored component (HC in this example) is introduced to the catalyst sample (time = 0). Storage occurs for 30 minutes, after which time the release step of the protocol is executed. For HC storage, release happens by removing the HC from the feed stream and beginning the 20°C/min thermal ramp.



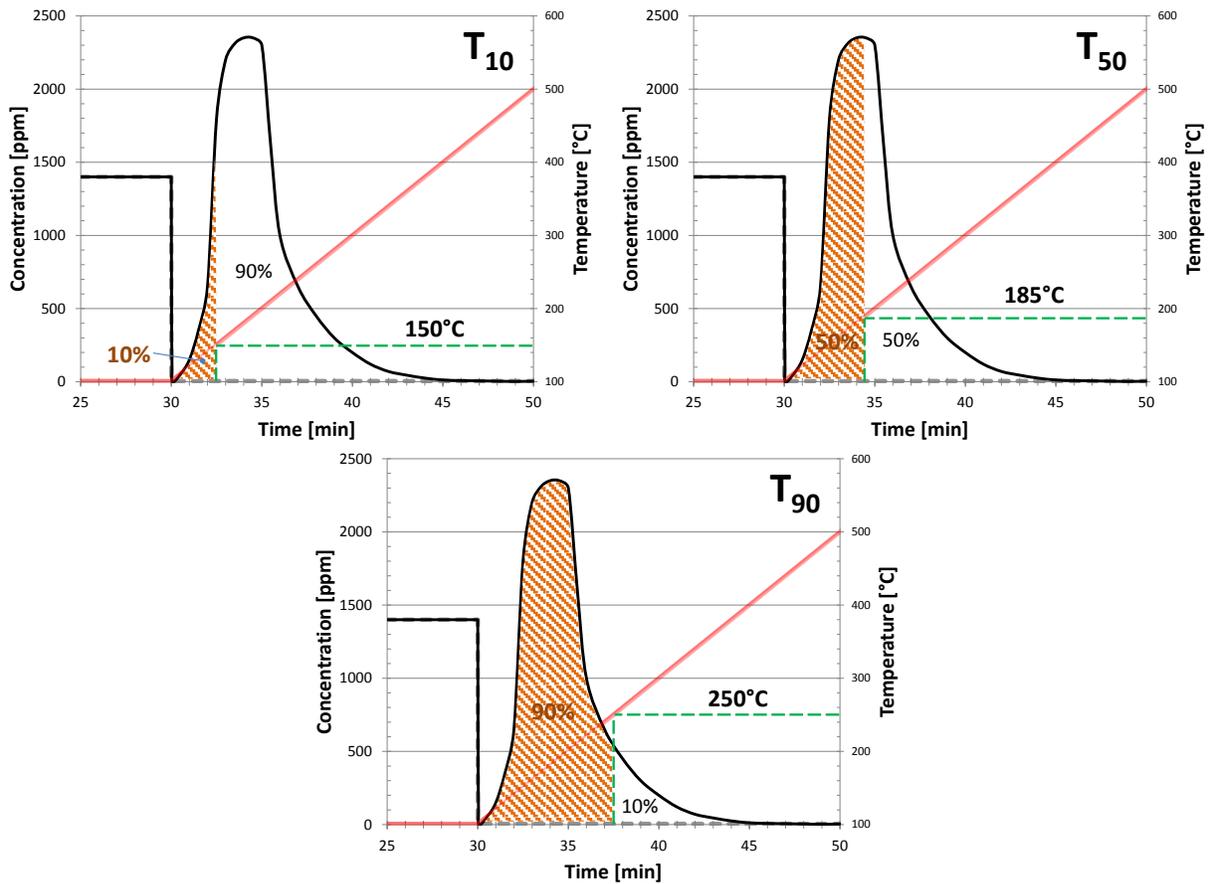
**Figure B1 – Illustrative example of HC storage (and release) protocol execution**

Following execution of the test, the concentration versus time data is added to Figure B1 to produce Figure B2 (left). The area above the concentration curve during the storage event is integrated to determine the total amount stored. Similarly, the area below the concentration curve during the release event is integrated to determine the total amount released. Figure B2 (right) is provided for illustrative purposes. This process is intended to provide information regarding the capacity of the catalyst for low-temperature storage; by comparing the cumulative integrated released versus stored amounts, this also provides information regarding the fraction of the stored component that is not released, and thus is assumed converted.

The set of information shown in Figure B3 (for illustrative purposes) is intended to provide information regarding the temperature at which the stored component is released from the catalyst. This is done by integrating and reporting the temperature at which 10% is released ( $T_{10}$ ), 50% is released ( $T_{50}$ ), and 90% is released ( $T_{90}$ ), in reference to the total amount that is released.



**Figure B2 – Illustrative example of HC storage capacity and release amount reporting**



**Figure B3 – Illustrative example of release temperature reporting**

## **APPENDIX C: POTENTIAL MODIFICATIONS**

For any modification, it is important to consider the validity of the aftertreatment process as being representative in the presence of the proposed exhaust modification. For this reason, it is best practice for the user to conduct sensitivity studies comparing catalyst performance in the presence and absence of the proposed simulated exhaust modification to insure catalyst insensitivity to the modification.

### Analytical Challenges

With certain analytical techniques, it may be necessary to make modifications to exhaust gas composition in order to achieve necessary analytical capability. An example of this is the employment of mass spectroscopy for exhaust gas composition, where resolution of CO from N<sub>2</sub> and resolution of N<sub>2</sub>O from CO<sub>2</sub> are prohibitively challenging. In the former case, for HC trap characterization, CO may be formed as a partial conversion product, and thus the user may choose to replace N<sub>2</sub> with an alternative inert diluent (e.g. Ar) to allow accurate CO detection. In the latter case, for PNA characterization, N<sub>2</sub>O may be formed as a byproduct, and thus the user may choose to omit CO<sub>2</sub> from the feed stream.

### Carbon Balancing

For HC trap characterization and effectively quantifying HC that is converted versus released, CO<sub>2</sub> analysis at low concentration may be warranted during the release event for carbon balancing. To do so requires CO<sub>2</sub> to be omitted from the feed stream during the release step. It is expected that the presence or absence of CO<sub>2</sub> in the feed stream has no significant effect on the adsorption, desorption, or reactive behavior of the catalyst.

If carbon balancing is performed by omitting CO<sub>2</sub> from the reactor feed stream, then CO<sub>2</sub> production should be accounted for when reporting the test results/performance data. It should be reported as a cumulative total to reflect the total amount of the stored component that was converted. It should also be combined with the total amount of HC C<sub>1</sub> released (cumulative and versus time) to reflect the total amount converted & released (cumulative and versus time). Comparison of the total amount of component stored versus the cumulative total converted & released provides the effectiveness of the carbon balance for the test. The time-resolved converted & released data provides a more accurate assessment of release characteristics of the catalyst. In this instance, the T<sub>10</sub>, T<sub>50</sub>, and T<sub>90</sub> values should reflect the temperatures at which 10%, 50%, and 90% of the HC is accounted for (i.e., converted & released), respectively, compared to the cumulative total amount converted & released.

### De-coupling Conversion and Release

For HC trap characterization, it may also be of interest to de-couple conversion and release characteristics of the catalyst. This may be performed by omitting O<sub>2</sub> from the feed stream during the release step of the protocol. In this situation, the test should be compared to the analogous test in the presence of O<sub>2</sub> for comparative evaluation of release characteristics of the catalyst.