

# ***Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation: Low-Temperature Three-Way 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 conditions/procedures that sufficiently capture catalyst technology's performance capability and are adaptable in various laboratories. This document details a three-way catalyst (TWC) testing protocol.

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## BACKGROUND

Catalyst based exhaust aftertreatment system 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 also addresses 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 three-way catalyst with oxygen storage. In this instance, test protocols for such a system would require multiple steps to adequately characterize both conversion and storage performance. Therefore, the method of characterization will differ as a function of the relative complexity required to adequately quantify performance.

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/>. The second test protocol, the *Low-Temperature Storage Catalyst Test Protocol*, is nearing completion and will be released to the technical communication shortly. This document presents the third test protocol, and is focused on characterizing low-temperature three-way catalyst (TWC) performance.

## 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 performance of candidate TWC technologies. Specifically, this protocol will assess the oxygen storage capacity (OSC), and the hydrocarbon (HC), CO, and NO<sub>x</sub> conversion efficiencies of candidate catalysts intended for effective control of exhaust emissions from conventional and advanced stoichiometric gasoline engines. 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. In the protocol, NO<sub>x</sub> is represented by NO since this is predominantly the form of NO<sub>x</sub> emitted from the engine. HC is simulated by the combination of ethylene (C<sub>2</sub>H<sub>4</sub>), propylene (C<sub>3</sub>H<sub>6</sub>) and propane (C<sub>3</sub>H<sub>8</sub>).

TWC technology has been developed to be solely applicable to stoichiometric gasoline engine aftertreatment. Thus, applicability of this test protocol is similarly applicable to only stoichiometric gasoline engine aftertreatment. TWC technology was developed to enable necessary emission reduction from stoichiometric combustion engines with exhaust that is continuously cycling between net fuel-rich and net fuel-lean conditions as a result of feedback control of the exhaust air-to-fuel ratio around stoichiometric conditions. Exhaust composition in relation to stoichiometry is governed by the air-to-fuel ratio (A/F) during combustion; A/F is quantitatively expressed by Lambda ( $\lambda$ ) which is defined by the ratio of actual A/F to the A/F at stoichiometric conditions during combustion. By definition,  $\lambda=1$  represents stoichiometric conditions,  $\lambda<1$  represents a fuel-rich reducing environment, and  $\lambda>1$  represents a fuel-lean oxidizing environment. Dithering is the term used to describe the exhaust composition cycling between lean and rich conditions during stoichiometric combustion, which typically occurs at frequencies ranging from 0.5 to 3 Hz on current production gasoline vehicles.

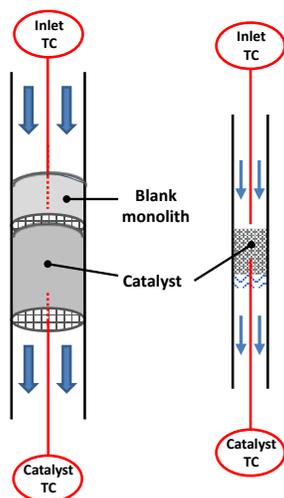
## REACTOR DESCRIPTION AND BEST PRACTICES

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

### 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 (13 mm) 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. The thermocouples should be metal sheathed exhibiting equivalent or superior thermal durability and chemical resistant properties as 316L stainless steel. A suggested maximum thermocouple diameter is 0.032 inch (~0.8 mm) to minimize adverse effects on flow dynamics, to avoid monolith damage as a result of thermocouple insertion, and to obtain to obtain sufficiently fast thermocouple response. For core sample 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 ensures the inlet thermocouple remain located

radially close to centerline and not in contact with the reactor wall, and (iii) the monolith provides improved flow distribution at the front face of the catalyst core sample.



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

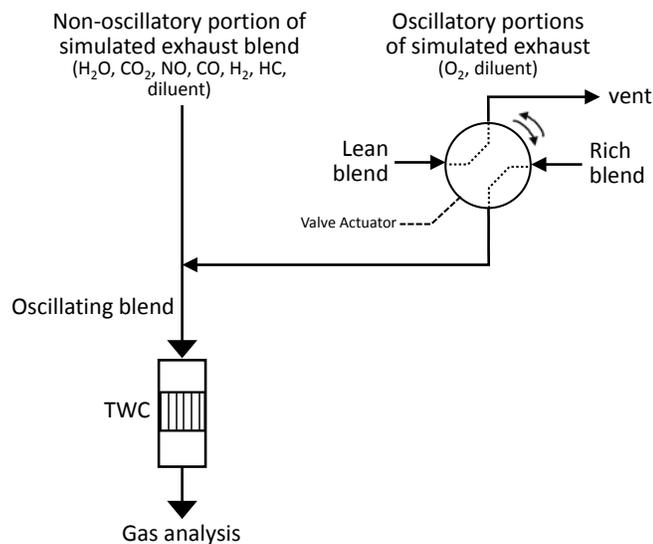
Chemical analysis capability should include, at a minimum, quantitative analysis of total hydrocarbon (HC), CO, NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, and CO<sub>2</sub>. It is preferable to have quantitative analysis of each specific HC species that is present in the simulated feed as well as CH<sub>4</sub>. However, a non-specific total HC analysis will suffice. For OSC measurement, it is imperative to have CO and/or CO<sub>2</sub> analysis capability accurate to at least 10 ppm to adequately resolve O<sub>2</sub> storage capacity. Analytical capability less than the minimum stated here will limit the usefulness and applicability of results. Although not required, O<sub>2</sub> and H<sub>2</sub> analysis is also encouraged for accurate TWC test method development and exhaust simulation. It is important to note that not all analytical methods provide the necessary measurement or resolution for emissions analysis. 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 5 ppm or lower is required for that component. Please note that preferable resolution of an emission measurement is ≤2% of feed concentration, and capability less than this will limit the usefulness and applicability of results.

For adequately characterizing oxygen storage capacity, the frequency of gas sample analysis is very important. The frequency of sample analysis will dictate the relative fidelity of the data used to determine the amount of stored oxygen. Therefore, best practice is a sampling frequency of 1 Hz. If sampling frequency is less than this then that should be reported with the data so that it can be considered with the data. This level of frequency will exclude chromatography-based O<sub>2</sub>/CO/CO<sub>2</sub> analysis techniques. If sufficient CO/CO<sub>2</sub> analysis capability is not available, the user may consider direct measurement of O<sub>2</sub> breakthrough for OSC characterization. This technique is not discussed in this document.

For tests employing temperature ramping for catalyst light-off characterization, important considerations include (i) frequency of gas sample analysis, and (ii) the rate of response. Regarding the rate of response, sufficiently fast analytical response is necessary to ensure measured performance is attributed to the correct catalyst temperature; this can be affected by many things, including sampling line volume (i.e., length & size), sampling flow rate, and various characteristics inherent to the analytical technique. It can be characterized by how quickly the analytical technique responds to a change in feed composition; a response time of ≤ 30 seconds is required to reach 90% of steady-state concentration following a step-change in feed composition. Regarding frequency of gas sample analysis, the desired

frequency of analysis will be dictated by the necessary resolution of data to adequately assess light-off behavior. This is set to a desired maximum of 10°C/sample. In most instances this is easily achieved using real-time gas analysis techniques (e.g., FT-IR, ND-IR, mass spectroscopy) or comparatively fast micro-GC analysis. However, this may be prohibitive in situations where the sample analysis rate is slow (e.g. some older chromatography-based analysis techniques). An example of this would be a 4-minute chromatography analysis method applied to a catalyst light off test employing a 5°C/minute ramp rate. In this situation, the user is acquiring 1 data point for every 20°C, which is less accurate than desired. In these instances, the thermal ramp used in the test can be slowed to facilitate necessary data resolution. In this example, it is suggested that the user slow the temperature ramp rate of the catalyst test to 2.5°C/minute or less to achieve 1 data point for every 10°C or less.

TWC testing of core and powder catalysts in Phase 2 is to include ‘dithering’, which is the simulation of the continuous cycling between net fuel-rich and net fuel-lean conditions in stoichiometric combustion engine exhaust. Adequately accomplishing dithering requires dedicated hardware for enabling an oscillating catalyst feed-stream composition. The catalyst feed stream will consist of the combination of a non-oscillatory portion of the flow, making up its majority (e.g., H<sub>2</sub>O, CO<sub>2</sub>, diluent), and an oscillatory portion of the flow (restricted to O<sub>2</sub>/N<sub>2</sub> in this protocol). The resulting blend will cycle between rich and lean conditions. The recommended frequency of oscillation (1 Hz) makes it prohibitive to adequately accomplish dithering of the oscillatory portion by flow rate adjustment or starting/stopping of individual component streams. Rather, its accurate simulation requires the use of two continuously-flowing lean & rich oscillatory streams (using diluent to match their total flow rate) and the strategic use of valves to quickly and repetitively switch (at the required frequency) between the two streams as the oscillatory portion of the catalyst feed-stream while the other stream is directed to vent. Figure 2 shows a simplistic example of how this can be achieved. See Appendix D for more details.



**Figure 2** – Schematic of system for ‘dithering’, i.e. creating an oscillating feed-stream composition.

**Catalyst Sample Requirements**

*Powder*

- Bed diameter (i.e. reactor ID) > 3 mm but < 13 mm

- Catalyst powder particle size can be as large as 600 micron (30 mesh) without causing significant internal diffusion resistances under typical TWC operating conditions, 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 between 19 mm and 25mm
- 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)  $\geq 1$
- High-temperature felt wrapped snugly around the core to eliminate flow bypassing

### **Reactor Performance Requirements**

#### *1. Minimizing thermal gradients*

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 gas 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. For powder catalysts, users have the option of diluting the catalyst sample with an inert material to minimize the contribution of exotherms.

#### *2. Reactor base-lining*

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 OSC measurements are transient in nature, it is also important to use reactor “base-lining” to characterize any equipment derived transients which may affect quantitative interpretation of time-resolved OSC data. Any equipment-derived transients should then be accounted for in the data analysis so that their presence does not misrepresent material performance.

#### *3. Dithering profile*

With dithering, it is important for the user to verify an acceptable dithering composition profile supplied to the catalyst inlet. An acceptable profile is one in which the apex of each  $\frac{1}{2}$ -cycle profile comes within  $\sim 5\%$  of reaching the steady-state condition of each respective stream. For additional details, see Appendix D.

### **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 appropriate 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  $\geq 150^{\circ}\text{C}$  to prevent condensation or absorption.
- If employing dedicated gas 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 still 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 OSC and conversion performance of candidate TWC technologies for stoichiometric GDI combustion (S-GDI, diluted with EGR). Conversion performance is characterized in the full simulated exhaust for the S-GDI application.  $[\text{O}_2]$  will vary in the test to simulate different lambda ( $\lambda$ ) values as shown in Tables 1(a) through 1(c). The difference between measured and targeted gas concentrations (from Table 1) should be  $\leq 10\%$ .

The standard space velocity to be employed is  $30,000 \text{ hr}^{-1}$  for monolith catalysts and  $200 \text{ [L/g-hr]}$  for powder catalysts. Optionally, a higher  $60,000 \text{ hr}^{-1}$  space velocity for monolith catalysts and  $400 \text{ [L/g-hr]}$  for powder catalysts can be adopted if more appropriate for the application or clearer discrimination among the candidate catalysts is desired.

The gas concentrations shown in Table 1 were selected by the authors to reflect the actual exhaust compositions for the S-GDI application. Therefore, it is important that these gas compositions (as well as the testing conditions described above) are followed when evaluating new catalyst materials. Omitting or significantly altering the components and concentrations identified in Table 1, or employing a lower space velocity than what is specified, will cast doubt on the ability of the catalyst to perform analogously to the data presented when evaluated on actual engines.

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

(a) – Lambda ( $\lambda$ ) = 0.97		(b) – Lambda ( $\lambda$ ) = 0.995		(c) – Lambda ( $\lambda$ ) = 1.02	
Constant components	$\lambda = 0.97$	Constant components	$\lambda = 0.995$	Constant components	$\lambda = 1.02$
[H <sub>2</sub> O]	13%	[H <sub>2</sub> O]	13%	[H <sub>2</sub> O]	13%
[CO <sub>2</sub> ]	13%	[CO <sub>2</sub> ]	13%	[CO <sub>2</sub> ]	13%
[NO]	1000 ppm	[NO]	1000 ppm	[NO]	1000 ppm
Variable components		Variable components		Variable components	
[O <sub>2</sub> ] <sup>(b)</sup>	0.12%	[O <sub>2</sub> ] <sup>(b)</sup>	0.64%	[O <sub>2</sub> ] <sup>(b)</sup>	1.15%
[CO]	0.50%	[CO]	0.50%	[CO]	0.50%
[H <sub>2</sub> ] <sup>(c)</sup>	0.17%	[H <sub>2</sub> ] <sup>(c)</sup>	0.17%	[H <sub>2</sub> ] <sup>(c)</sup>	0.17%
Hydrocarbon [HC]		Hydrocarbon [HC]		Hydrocarbon [HC]	
total	3000 ppm C <sub>1</sub>	total	3000 ppm C <sub>1</sub>	total	3000 ppm C <sub>1</sub>
[C <sub>2</sub> H <sub>4</sub> ]	525 ppm	[C <sub>2</sub> H <sub>4</sub> ]	525 ppm	[C <sub>2</sub> H <sub>4</sub> ]	525 ppm
[C <sub>3</sub> H <sub>6</sub> ]	500 ppm	[C <sub>3</sub> H <sub>6</sub> ]	500 ppm	[C <sub>3</sub> H <sub>6</sub> ]	500 ppm
[C <sub>3</sub> H <sub>8</sub> ]	150 ppm	[C <sub>3</sub> H <sub>8</sub> ]	150 ppm	[C <sub>3</sub> H <sub>8</sub> ]	150 ppm

- (a) Balance  $\text{N}_2$   
 (b) =  $f(\lambda)$   
 (c)  $[\text{H}_2]$  varied at 1/3 of  $[\text{CO}]$

**PROTOCOL EXECUTION**

The protocol should only be executed on a catalyst that has been, at a minimum, fully calcined and de-greened. It is requested that the user test catalysts following de-greening, following thermal aging, and following sulfur poisoning. See DE-GREENING AND AGING for more information.

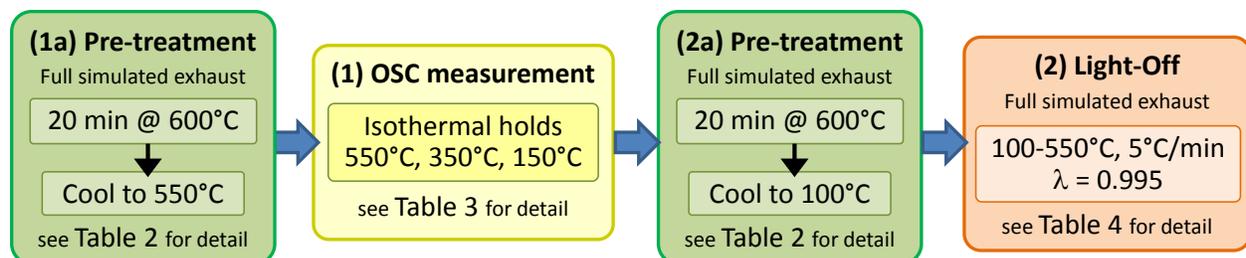
This protocol is unique in that a staged approach is presented for catalyst testing to facilitate high-throughput screening of powder catalysts at fixed lambda ( $\lambda$ ) conditions, followed by testing under dithering conditions for the candidate catalysts that show merit for further evaluation. The user has the option of skipping Phase 1 testing and proceeding directly to Phase 2 testing with powder or core samples, if desired. The steps for testing powder and core catalysts are detailed below.

As shown in Figures 3 through 5, protocol execution consists of the following steps:

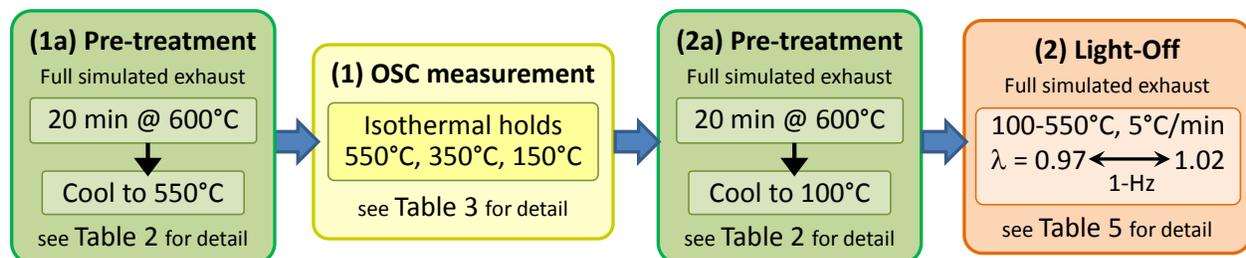
- Step 1a *Pre-treatment* to ensure common conditions prior to OSC measurement.
- Step 1 Three sequential *isothermal holds* at 550°C, 350°C, and 150°C for OSC measurement.
- Step 2a *Pre-treatment* to ensure common conditions prior to light-off measurement.
- Step 2 A 5°C/min *thermal ramp* from 100°C to 550°C for characterizing catalyst light-off behavior in the full simulated exhaust.

Powder and core catalyst testing is to be conducted in two (2) phases

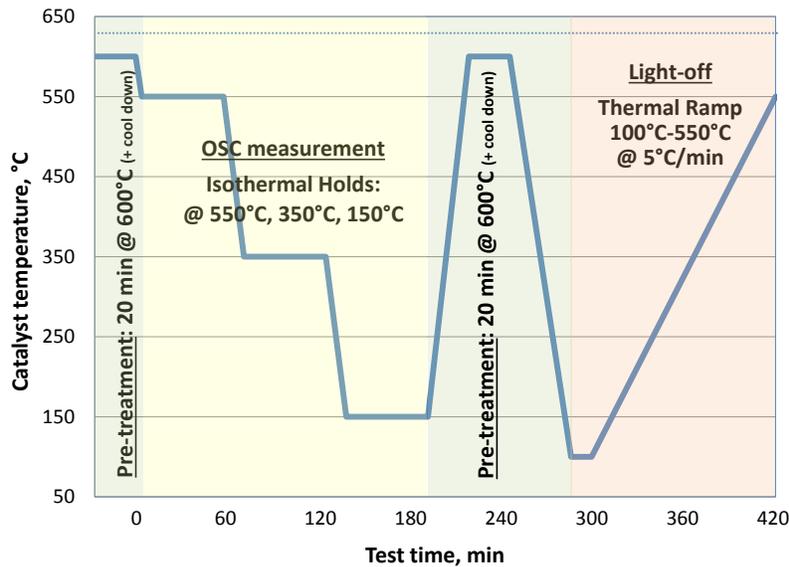
- Phase 1 – The full-simulated exhaust used in Step 2 is at a fixed lambda ( $\lambda$ ) = 0.995 shown in Table 1(b), reflecting slightly rich conditions. This is optional for core catalysts.
- Phase 2 – The full-simulated exhaust used in Step 2 is a 1-Hz oscillating feed stream composition simulating dithering between  $\lambda = 0.97$  and  $1.02$  shown in Tables 1(a) and 1(c), respectively.



**Figure 3 – TWC protocol test strategy – Phase 1 (without dithering, optional for cores)**



**Figure 4 – TWC protocol test strategy – Phase 2 (with dithering)**



**Figure 5** – TWC protocol temperature control, Phases 1 and 2 testing (illustrative purposes only; actual test times may vary).

Pre-treatment

Table 2 provides the details of the protocol pre-treatment steps, and is the same for each pre-treatment and for powder and core catalysts. Pre-treatment is performed to ensure that common conditions prevail prior to catalyst performance characterization; it consists of heating the catalyst to 600°C and holding for 20 minutes in the full simulated exhaust shown in Table 1(b) for  $\lambda=0.995$ .

**Table 2** – Step 1a and Step 2a of protocol: Pre-treatments (all catalysts)

PRE-TREATMENT – S-GDI								
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>						
TWC-PT	Pretreat 20 min @ 600°C	[HC]	[CO]	[H <sub>2</sub> ]	[NO]	[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]

<sup>(a)</sup> Bracketed concentration values are found in Table 1(b)

Isothermal Holds – 550°C, 350°C, 150°C

Table 3 provides detail for the isothermal hold steps of the protocol, and is the same for powder and core catalysts. OSC is measured at each isothermal hold temperature as follows:

- (1) Cool catalyst to isothermal hold temperature in inert (N<sub>2</sub>)
- (2) Add 1.5% O<sub>2</sub> only and hold isothermally for 10 minutes to stabilize temperature and saturate OSC, measuring [O<sub>2</sub>] in the effluent if feasible.
- (3) Omit O<sub>2</sub> (i.e., flowing only N<sub>2</sub>) and pause for 30 seconds
- (4) Add 0.2% CO\*\* only and measure CO and CO<sub>2</sub> concentration in effluent, 5 minutes minimum

**\*\*NOTE:** Only O<sub>2</sub> and CO should be used in Steps 2 and 4 above, respectively. Any other components (e.g., H<sub>2</sub> with CO) will introduce error in the measurement and should be omitted. Additionally, it is strongly suggested that the user have solenoid valves to switch between continuously flowing O<sub>2</sub> and CO streams while venting the other to improve accuracy (verses turning mass flow controllers ON/OFF).

Quantifying the fraction of O<sub>2</sub> retained on the catalyst by its breakthrough curve provides a direct assessment of its OSC. If this is not feasible, quantifying the total amount of CO converted to CO<sub>2</sub> provides a reliable assessment of the OSC of the catalyst. Please note that CO<sub>2</sub> sensitivity and accuracy at low concentration will be required for adequate OSC measurement in this fashion. OSC should be reported as a normalized value on a mass basis for powder catalysts [i.e., mg-O<sub>2</sub>/mg-catalyst] and a volume basis for coated monolith catalysts [i.e., mg-O<sub>2</sub>/L-catalyst]. See Appendix B for more detail.

**Table 3 – Step 1 of protocol: Isothermal Holds (all catalysts)**

<b>OSC Measurement @ 550°C, 350°C, 150°C</b>								
<b>Step No.</b>	<b>Temperature</b>	<b>Exhaust make-up (balance N<sub>2</sub>)<sup>(a)</sup></b>						
TWC-OSC-1	Cool to isothermal hold temperature	-	-	-	-	-	-	-
TWC-OSC-2	Saturate OSC 10 minutes	-	-	-	-	1.5% O <sub>2</sub>	-	-
TWC-OSC-3	OSC measurement ≥ 5 minutes	-	-	-	0.2% CO	-	-	-

<sup>(a)</sup> OSC measurement is performed using the simple shown for the given Step No. No other components should be used during the measurement other than inert diluent (N<sub>2</sub>).

Thermal Ramp

Table 4 provides detail for Step 2, the thermal ramp portion of the protocol, in Phase 1 testing without dithering. It is performed as follows:

- (1) Cool to 100°C and stabilize inlet in the full simulated exhaust in Table 1(b), λ=0.995.
- (2) Ramp from 100°C to 550°C at 5°C/min.

All temperatures refer to the catalyst inlet temperature. During the thermal ramp, HC, CO, and NO<sub>x</sub> conversion performance is measured as a function of temperature (at slightly rich conditions, i.e., λ=0.995).

**Table 4 – Step 2 of protocol: Thermal Ramp, Phase 1 (without dithering, optional for cores)**

<b>Light-Off Characterization</b>								
<b>Step No.</b>	<b>Temperature</b>	<b>Exhaust make-up (balance N<sub>2</sub>)<sup>(a)</sup></b>						
TWC-LO1-1	Cool to 100°C, Stabilize Inlet	[HC]	[NO]	[CO]	[H <sub>2</sub> ]	[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]
TWC-LO2-2	Ramp 5°C/min to 550°C	[HC]	[NO]	[CO]	[H <sub>2</sub> ]	[O <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]

<sup>(a)</sup> Bracketed concentration values are found in Table 1(b) representing λ=0.995.

Table 5 provides detail for Step 2, the thermal ramp portion of the protocol, in Phase 2 testing with dithering. It is performed as follows:

- (1) Stabilize inlet at 100°C with full simulated exhaust dithering composition at 1 Hz between λ = 0.97 and 1.02.
  - i.e., oscillating [O<sub>2</sub>] every 0.5 seconds between λ = 0.97 and λ = 1.02 for a 1-Hz total cycle frequency, with values found in Tables 1(a) and 1(c).
  - It is important to note that both oscillating exhaust streams should be the same total flow rate; see Appendix D for more detail.
- (2) Ramp from 100°C to 550°C at 5°C/min in the full simulated exhaust with dithering.

All temperatures during the test portion of the protocol refer to the catalyst inlet temperature. During the thermal ramp, HC, CO, and NO<sub>x</sub> conversion performance is measured as a function of temperature.

**Table 5 – Step 2 of protocol: Thermal Ramp, Phase 2 (with dithering)**

<b>Light-Off Characterization</b>						
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>				
TWC-LO2-1	Cool to 100°C <sup>(b)</sup> , Stabilize Inlet	[HC]	[NO]	[CO]	[H <sub>2</sub> ]	[O <sub>2</sub> ] = $f(\lambda)$ $\lambda = 0.97 \leftrightarrow 1.02$ @ 1-Hz
		[CO <sub>2</sub> ]	[H <sub>2</sub> O]			
TWC-LO2-2	Ramp 5°C/min to 550°C	[HC]	[NO]	[CO]	[H <sub>2</sub> ]	[O <sub>2</sub> ] = $f(\lambda)$ $\lambda = 0.97 \leftrightarrow 1.02$ @ 1-Hz
		[CO <sub>2</sub> ]	[H <sub>2</sub> O]			

<sup>(a)</sup> Bracketed concentration values are found in Tables 1(a) and 1(c).

<sup>(b)</sup> Feed can be cooled without dithering at  $\lambda = 0.995$  found in Table 1(b).

### DE-GREENING AND AGING

The protocol should only be executed on a catalyst that has been, at a minimum, de-greened to ensure 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 (not covered in this document), 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 routine protocol test strategy. Rather, it should be done prior to activity characterization. It is important to note that he 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, and are unique to the TWC application. 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, followed by chemical poisoning (i.e., in sequential fashion), with the test protocol conducted following each treatment. Chemical poisoning by engine oil (e.g., P) is not addressed here.

#### Catalyst De-greening

The de-greening conditions are shown in Table 6, and consist of neutral conditions (10% CO<sub>2</sub>, 10% H<sub>2</sub>O, balance N<sub>2</sub>) for the S-GDI gasoline application. The de-greening procedure consists of exposing the catalyst to the gas mixture and ramping from room temperature to 700°C temperature 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 6 – Catalyst de-greening parameters (all catalysts)**

<b>S-GDI</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]
TWC-DG	Neutral	700°C/4 hours	-	10%	10%

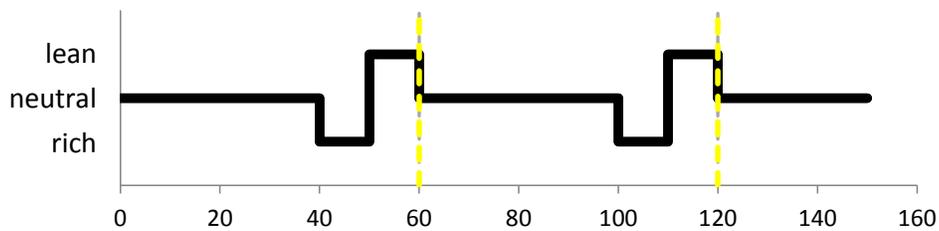
#### Catalyst Thermal Aging

Thermal aging representative of anticipated in-use durability requirements is to consist of 50 hours continuous operation at a constant inlet temperature which achieves  $\geq 900^\circ\text{C}$  peak mid-bed catalyst temperature at the start of aging. As detailed in Table 7 and Figure 6, the stoichiometric gasoline combustion application 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. Users should conduct only a single 50-hour aging cycle per catalyst. In contrast to de-greening, the temperature noted above for thermal aging (900°C) refers to the peak catalyst *bed* temperature as opposed to the inlet temperature. Although the aging cycle is close to thermally-neutral, there may be a small exotherm associated with it. Thus, there will be some method development required of the user to ensure 900°C is reached during the aging cycle.

**Table 7** – Catalyst aging cycle parameters for TWC application

S-GDI							
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> ]
TWC-AG-N	Neutral	40 seconds	-	10%	10%	-	-
TWC-AG-R	Rich	10 seconds	-	10%	10%	3%	1%
TWC-AG-L	Lean	10 seconds	3%	10%	10%	-	-

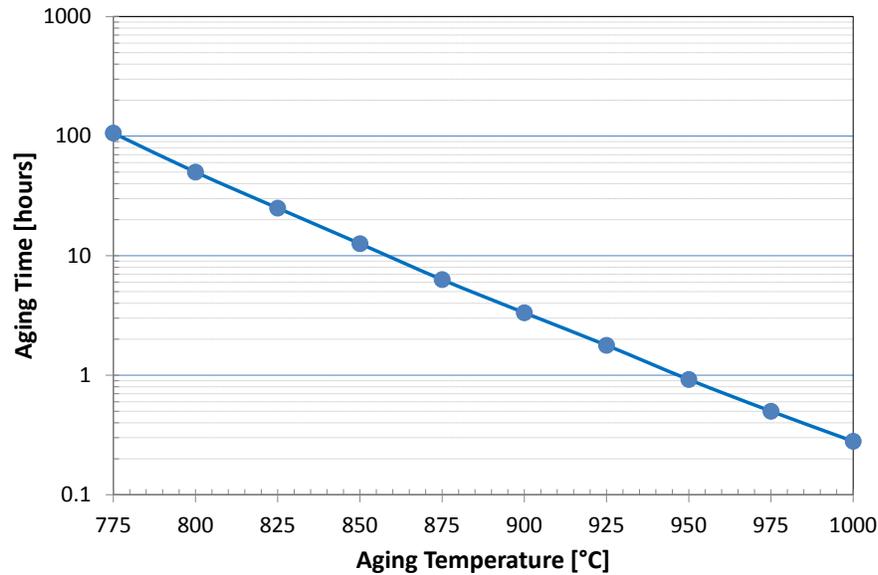


**Figure 6** – Catalyst aging cycle for TWC application

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. Figure 7, provided for illustrative purposes only, shows an example of the relationship between equivalent aging hours and temperature. 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  $\pm 5^\circ\text{C}$  of the desired temperature. Additionally, it is important to note that the aging temperature is based on the catalyst inlet thermocouple rather than bed thermocouple, since the former is more conducive to stable and repeatable operation.

### Aging Time and Temperature Relationship



**Figure 7** – Aging hours as a function of aging temperature to provide equivalent deterioration (for illustrative purposes only)

#### Transitory 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 Step 1a, the initial OSC pre-treatment, and cooling to 300°C under the full exhaust mix ( $\lambda = 0.995$ ). Following sulfur exposure, SO<sub>2</sub> is to be removed from the feed and the sample heated to 550°C under neutral conditions at which point the remainder of the protocol is to be executed.

**Table 8** – Catalyst poisoning parameters (all catalysts)

S-GDI									
Step No.	Temperature	Exhaust make-up (balance N <sub>2</sub> ) <sup>(a)</sup>							
TWC-PT-S1	<b>Pretreat</b> 20 min, 600°C	[NO]	[CO]	[H <sub>2</sub> ]	[HC]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-
TWC-PT-S2	<b>Cool</b> 600°C – 300°C	[NO]	[CO]	[H <sub>2</sub> ]	[HC]	[O <sub>2</sub> ]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-
TWC-PT-S3	<b>Poison</b> 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>
TWC-PT-S4	<b>Heat</b> 300°C – 550°C	-	-	-	-	-	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	-

<sup>(a)</sup> Bracketed concentration values are found in Table 1(b)

## 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, etc.
- 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, including:

- PGM loadings
- PGM dispersion, if known
- Ceria loading & other promotors

### **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
- Hardware used for oscillating the feed-stream composition
- Chemical analysis technique(s) and instrumentation used (e.g., Nicolet 6700 FTIR with 190°C heated gas cell)
- 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

### **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.

- Confirmation that the intended engine application/combustion strategy is gasoline stoichiometric combustion
- 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 6 and 7. If they are not different, then referencing the applicable table(s) is sufficient

- The procedures used for pre-treating or poisoning the catalyst(s) and measuring performance, including feed gas compositions, flowrate, pre-treatment and isothermal hold temperatures and hold times, and ramp rate, if they are different than those specified in Tables 1 through 3, 4 or 5, and 7. Again, if they are not different, then referencing the applicable table(s) is sufficient

### ***Test Results/Performance Data***

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

#### O<sub>2</sub> storage

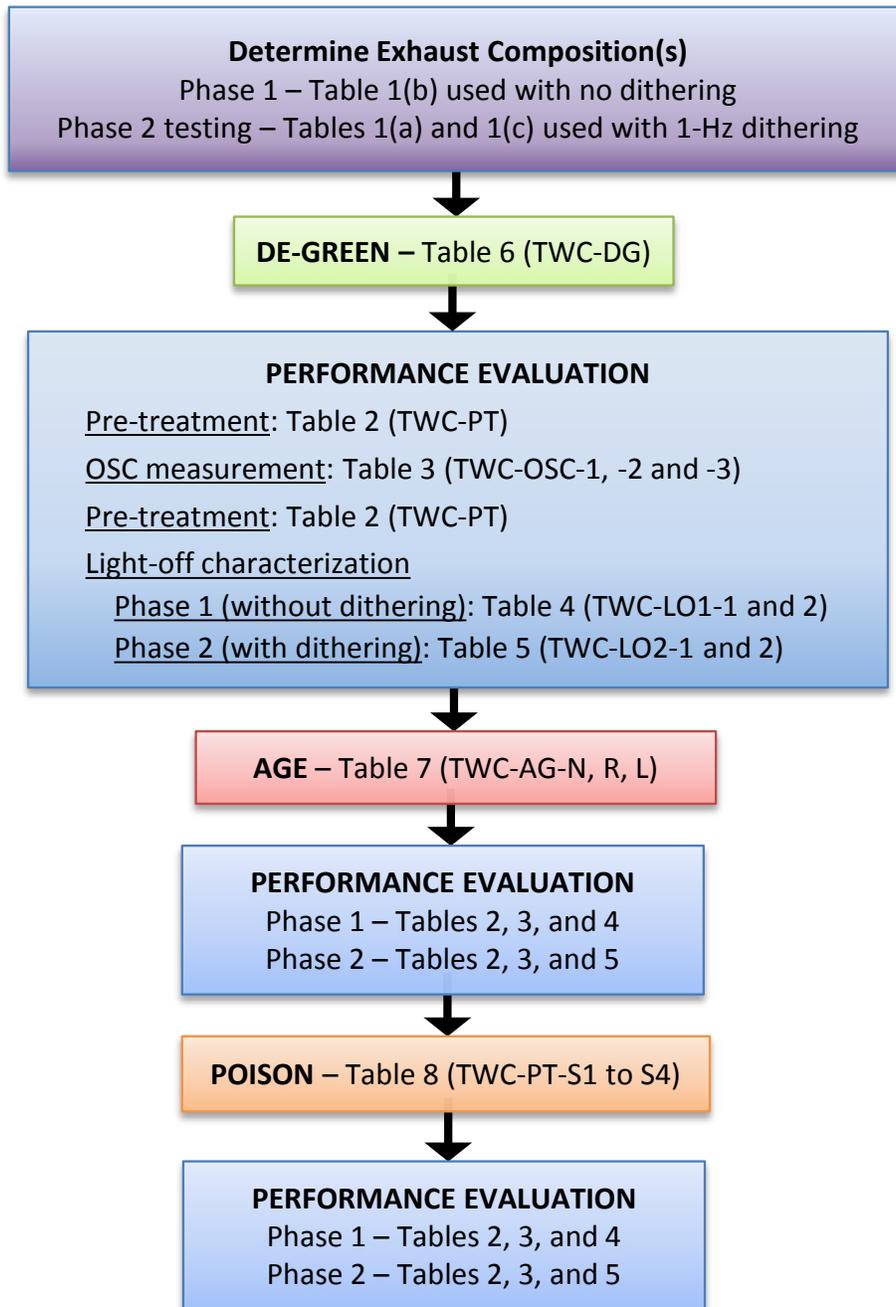
- The amount of O<sub>2</sub> storage measured at 550°C, 350°C and 150°C
  - Powder catalysts – [## mg-O<sub>2</sub>/mg-catalyst]
  - Core catalysts – [## mg-O<sub>2</sub>/L-catalyst]
- It is also suggested that the user provide traces of [CO] and [CO<sub>2</sub>] measured versus time (and [O<sub>2</sub>] if measured) for the OSC measurement steps (Step No. TWC-2-O in Table 3).

#### Conversion Performance

- Measured inlet and outlet concentrations of NO, CO, and HC (preferably each individual HC as well as total HC) and outlet concentrations of NO<sub>2</sub>, N<sub>2</sub>O, and NH<sub>3</sub>, with the associated catalyst inlet temperature and catalyst bed (or monolith) temperature. Also include measured inlet and outlet concentrations of O<sub>2</sub> if available.
- Conversion efficiency of NO, CO and HC as a function of both catalyst inlet and catalyst bed temperature, preferably in graphical format.
- T50 and T90 determination, referencing catalyst inlet temperature, for NO, CO, and HC.

**APPENDIX A: PROTOCOL FLOW CHART**

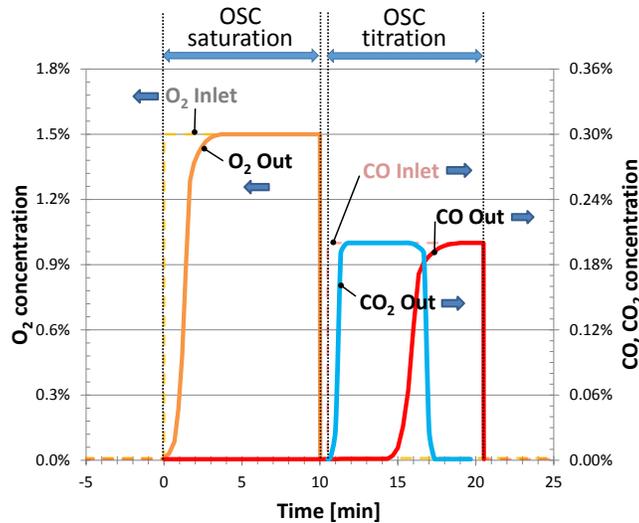
It is suggested that the user conduct catalyst testing in the order as it appears in Figure A1 below. If the user wishes to test aged catalysts only, then aging can be conducted without requiring an initial de-greening.



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

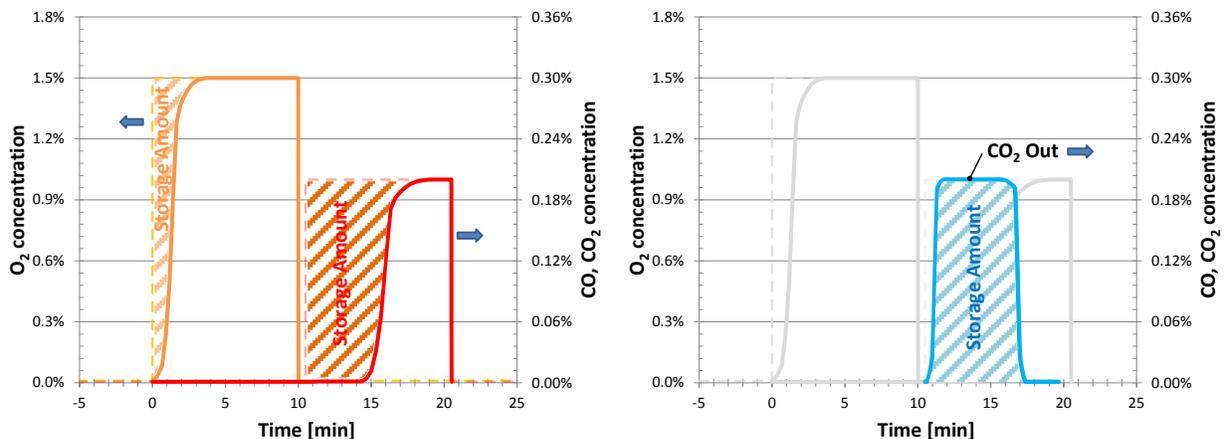
**APPENDIX B: PERFORMANCE DATA**

The test portion of the protocol includes both OSC and light-off (i.e., conversion) performance measurement in Steps 1 and 2 of the protocol, respectively. As a transient measurement, accurately reporting OSC from the protocol includes graphically reporting the data ([CO], [CO<sub>2</sub>], and/or [O<sub>2</sub>]) as a function of time. As shown in Figure B1 (for illustrative purposes only), [O<sub>2</sub>] and [CO] will be breakthrough curves during the saturation and titration steps of OSC measurement, respectively, and [CO<sub>2</sub>] will be peak produced during the titration step of the protocol.



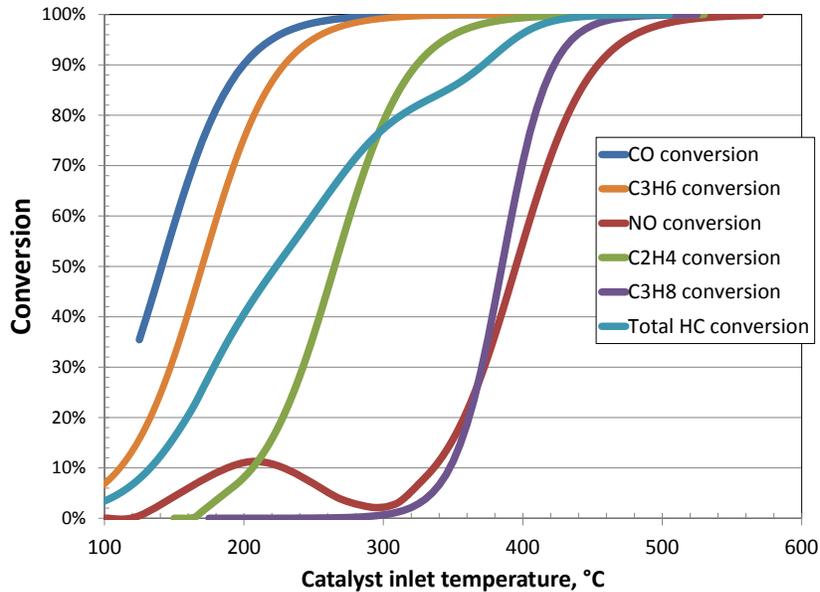
**Figure B1** – O<sub>2</sub>, CO, and CO<sub>2</sub> curves during Step 1 of the protocol (illustrative only)

The OSC of the catalyst can be measured by integrating the area above the [O<sub>2</sub>] curve or the [CO] curve, as shown in Figure B2 (left). However, it is important to note that each reactor system will have a blank transient response for [O<sub>2</sub>] and [CO] that must be properly corrected for using this method. The OSC of the catalyst can also be measured by integrating the area under the [CO<sub>2</sub>] as shown in Figure B2 (right). This method, in contrast, requires no blank system response correction. It is best practice to conduct the OSC measurement on a catalyst multiple times until a repetitive stable result is achieved.

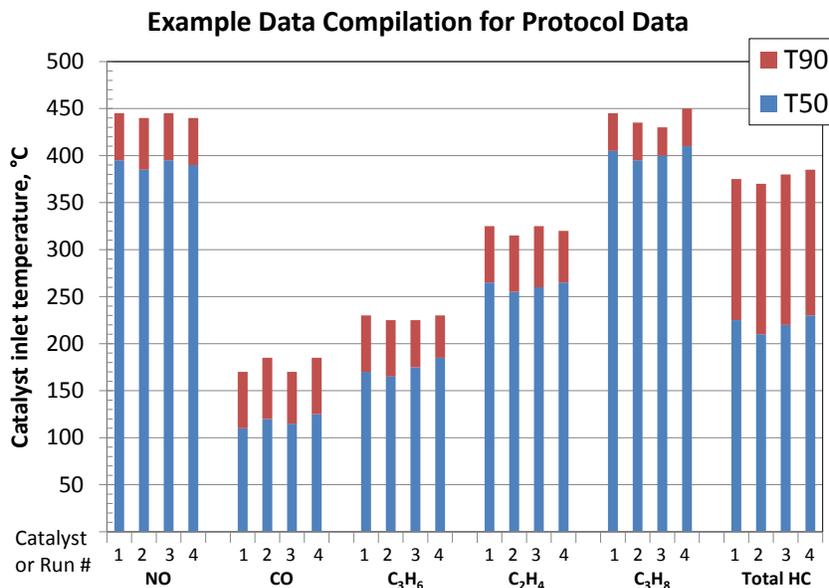


**Figure B2** – OSC measurement by integrating [O<sub>2</sub>], [CO] or [CO<sub>2</sub>] curves (illustrative only)

The light-off portion of the protocol in Step 2 is intended to generate a set of CONVERSION versus TEMPERATURE data analogous to Figure B3 below (illustrative only). Comparing the results of multiple protocol tests (e.g. investigating catalyst performance sensitivity to test parameters, or comparing the results of multiple catalysts) is most easily accomplished by extracting T50 and T90 data (temperature at which a component reaches 50% and 10% of its feed concentration, respectively) and presenting in column format. This is shown in Figure B4 below (illustrative only) for an example of four (4) successive protocol tests.



**Figure B3** – Illustrative example of conversion versus temperature data for TWC testing



**Figure B4** – Illustrative example of T50 & T90 data for TWC testing

## **APPENDIX C: POTENTIAL MODIFICATIONS OF FEEDSTREAM COMPOSITION**

For any modification, it is important to consider the validity of the aftertreatment process as being representative in the presence of the proposed exhaust composition 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 composition modification to ensure 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, the user may choose to replace N<sub>2</sub> with an alternative inert diluent (e.g. Ar) to allow accurate CO detection; alternatively, the user may choose to omit CO<sub>2</sub> from the simulated exhaust feed to allow accurate CO<sub>2</sub> detection at [ppm] level in the catalyst effluent as a strategy for indirectly quantifying CO oxidation. In the latter case, the situation is more complex, as resolution of N<sub>2</sub>O from CO<sub>2</sub> with mass spectrometry is not readily feasible. This requires the user to replace N<sub>2</sub> with an alternative diluent to allow accurate N<sub>2</sub> detection at the [ppm] level; the discrepancy in the N-balance could then be attributed to N<sub>2</sub>O. However, employment of this strategy would preclude the inclusion of CO in the test matrix due to the interfering effect on N<sub>2</sub> analysis.

### Selectivity, Nitrogen Balancing, and Carbon Balancing

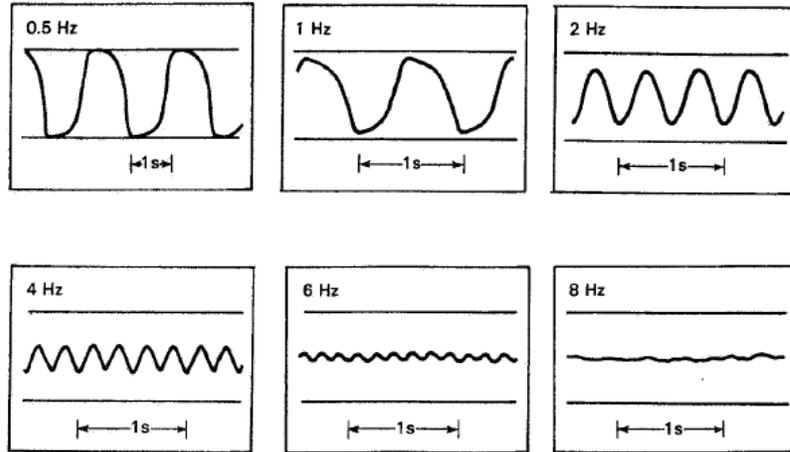
In its most simplistic form, the protocol defines conversion during light-off characterization as the disappearance of a component. However, selectivity can be a significant contributing factor for accurate TWC assessment. It is important to understand the fate of NO conversion to NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, or N<sub>2</sub>. The latter (N<sub>2</sub>) can be determined by inference based upon analysis of the other four components, or it can be measured directly by replacing N<sub>2</sub> with an alternative inert diluent (e.g. Ar). Similarly, under certain conditions, HC can undergo partial conversion (e.g. partial oxidation, cracking) as opposed to complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O. In this situation, the disappearance of HC in the feed and the oxidation of HC to CO<sub>2</sub> would see a divergence. Characterizing all potential partial-conversion products is not practical, which leads to potential modification of the protocol to include carbon balancing. Carbon balancing characterizes partial conversion products as a lump total, and is most efficiently conducted by omitting CO<sub>2</sub> from the simulated exhaust feed. Omitting CO<sub>2</sub> from the feed allows the user to measure CO<sub>2</sub> at the [ppm] level in the effluent; the discrepancy in the C<sub>1</sub>-balance can then be attributed to products of partial conversion as a lump sum.

## APPENDIX D: HARDWARE FOR ACCURATELY OSCILLATING FEED-STREAM COMPOSITION

Adequate simulation of engine exhaust under A/F dithering during combustion requires dedicated hardware for enabling an oscillating feed-stream composition. Figure 2 shows a simplistic example of how this can be achieved at the recommended frequency of oscillation (1 Hz). Additionally, some important notes for the necessary hardware and catalyst include:

- It is not suggested to oscillate two fully-formulated simulated exhaust streams. Rather, only part of the exhaust components should be oscillated and subsequently combined with the non-oscillatory portion of the simulated exhaust stream. In this protocol, only O<sub>2</sub> (and N<sub>2</sub> as diluent) should be in the oscillatory stream, with the balance of components and N<sub>2</sub> in the non-oscillatory stream.
- To achieve composition oscillation, the strategic use of valving should be employed to switch between the two lean/rich streams as the oscillatory portion of catalyst feed-stream while directing the other exhaust stream to vent. The simplest configuration is to use a 4-port two-position fast switching valve which is shown in Figure 2. In this example, the valve would rotate ¼-turn every 0.5 seconds for re-directing the two streams.
- Both lean/rich oscillating streams should be fully-developed, continuously flowing, and the same flow rate. There should be no transient flow-rate adjustment or the starting/stopping of individual component streams.
- It can help to direct part of the bulk diluent (e.g., N<sub>2</sub>) with the oscillatory stream to improve bulk mixing. Additionally, if the flow rate of the oscillatory portion of the exhaust is different then diluent will be required to match their total flow.
- To prevent pulsation effects, the back-pressure to vent and back-pressure to catalyst should be matched to each other between the two lean/rich oscillating streams.
- To achieve an adequate dithering profile, it is important for the apparatus to minimize the degree of blending between the two oscillating feed-stream compositions prior to catalyst exposure. This means that the distance between feed-stream switching and the catalyst bed should be minimized, along with the associated dead volume within.
- Minimizing blending also means that a total flow rate of at least ~2 SLPM must be used. For core samples this is not an issue. However for powder catalysts, this requires a catalyst sample size of at least 600 mg, which is larger than what is typically used in powder catalyst testing. With this amount of catalyst, the required pressure drop to flow 2 SLPM through the bed can become prohibitive. This effect can be mitigated by (1) increasing the diameter of the powder catalyst bed, (2) pressing, crushing, and sieving the catalyst to a particle size of 30 mesh (0.6 mm) to 100 mesh (0.15 mm), or combinations thereof.
- It is requested that the user verify an acceptable dithering composition profile at the catalyst inlet. To characterize dithering composition profile for a test system, the user can use a hot-wire anemometer. Hot wire anemometers, although originally designed to monitor flow rate, can measure the sinusoidal profile of an oscillating feed stream in a similar fashion. Additional means of measuring dithering efficacy are mass spectroscopy or a wide-range O<sub>2</sub> sensor, both of which are acceptable with adequate data resolution (# of data points per time span).
- An acceptable dithering profile is one in which the apex of each ½-cycle profile comes within ~5% of reaching the steady-state condition of each respective stream. Figure D1 shows sample hot-wire anemometer traces from dithering profiles for a system at various cycle frequencies. For the example provided here, a 1 Hz cycle frequency is the fastest acceptable profile to be used.

Increasing the cycle frequency to 2 Hz results in a cycle apex that stops ~20% short of the steady-state condition, and thus is unacceptable.



**Figure D1** – Hot-wire anemometer traces from dithering profiles at various cycle frequencies. Horizontal lines show the steady-state hot-wire anemometer outputs for the separate streams.