Trimble County IRM Calibration/Spiking Experiments

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A series of experiments to perform the procedures outlined in the "conceptual" mercury (Hg) instrumental reference method (IRM) was conducted at the Trimble County Hg continuous emissions measurement system (CEMS) site. The Tekran Model 2537 system was used as the IRM system, since, currently, that is the only system at Trimble County that measures the probe loop flow rate with a calibrated measurement device (i.e., a venturi). During this attempt at performing IRM checks, the sample probe was in a fixed, installed position and was ***not*** traversed.

The initial step in conducting the IRM pre-test system checks is to perform a three-level elemental Hg calibration error check. This was performed by first injecting a high-level calibration gas in the normal location upstream of the inertial filter, with probe loop flow rate lowered to 15 liters per minute (lpm). Once a stable response was achieved, the instrument readings were adjusted by changing the calibration factor(s) until the system response was ~10.0 micrograms per standard cubic meter (µg/scm). This is the normal daily calibration check/adjustment procedure. After adjusting the high-level response, the system was challenged at the mid- and low-levels without any adjustment to the calibration factors. The IRM performance criteria for the elemental Hg calibration error check is either a difference of less than or equal to 2% of span or an absolute difference less than or equal to 0.2 µg/scm at each calibration gas level. Table 1 provides a summary of the elemental calibration error results.

Table 1: Summary of Elemental Hg Calibration Error Check – August 28, 2006

Elemental Hg Calibration Error Check						
Calibration Gas Level	Reference Value (ug/m^3)	Verification Gas Level	Analyzer Response (ug/m^3)	Difference (ug/m^3)	Cal Error % of Span (%)	Cal Error Status
Low	2.52	LOW	2.56	0.0	0.4%	PASS
Mid	5.03	MID	4.97	-0.1	-0.6%	PASS
High	10.00		10.04	0.0	0.4%	PASS

The next step in performing the IRM pre-test system checks is to perform a three-level system integrity check. The Hovaquick was used to produce the oxidized Hg calibration gases for this test. No adjustments were made to the calibration factors during the three-level system integrity check. The probe loop flow rate for the Tekran system was lowered to ~10 lpm during the three-level system integrity check. The performance criteria for the three-level system integrity check is either a difference of less than or equal to 5% of span or an absolute difference less than or equal to 0.5 µg/scm at each calibration gas level. Table 2 provides a summary of the three-level system integrity check.

Table 2: Summary of Three-level System Integrity Check – August 28, 2006

Oxidized Hg Calibration Error Check						
Calibration Gas Level	Reference Value (ug/m^3)	Verification Gas Level	Analyzer Response (ug/m^3)	Difference (ug/m^3)	Cal Error % of Span (%)	Cal Error Status
Low	2.35	LOW	2.46	0.1	1.1%	PASS
Mid	4.70	MID	4.54	-0.2	-1.6%	PASS
High	9.98		9.61	-0.4	-3.7%	PASS

The Tekran system was able to meet the criteria for the initial calibration checks, and the system was left to sample stack gas overnight before any attempts to conduct the pre-test dynamic spikes.

August 29, 2006

We were prepared to conduct the pre-test dynamic spike checks on the morning of August 29th, but the unit went offline overnight. With the unit offline, the stack gas readings on the Tekran were stable at ~0.5 µg/scm. Given the relative stability of the stack concentration readings, a check of system calibration error was conducted to check the status of the system in order to attempt practice dynamic spike checks. The system's response to the high elemental calibration gas required an adjustment to the calibration factors in order to meet the pre-test calibration error specifications. The system was recalibrated using the same procedures as detailed above. Table 3 provides a summary of the elemental Hg calibration pre-test performed on August 29, 2006.

Table 3: Summary of Elemental Hg Calibration Error Check – August 29, 2006

Elemental Hg Calibration Error Check						
Calibration Gas Level	Reference Value (ug/m^3)	Verification Gas Level	Analyzer Response (ug/m^3)	Difference (ug/m^3)	Cal Error % of Span (%)	Cal Error Status
Low	2.52	LOW	2.62	0.1	1.0%	PASS
Mid	5.03	MID	5.14	0.1	1.1%	PASS
High	10.00		10.09	0.1	0.9%	PASS

After completing the elemental Hg calibration error check, a practice high-level dynamic spike test was performed (Note: In accordance with the IRM, a 3-level oxidized system integrity check should have been performed before attempting the dynamic spike tests.) A total of three dynamic spike tests were performed over a period of ~90 minutes. The dynamic spike was performed by injecting an oxidized calibration gas from the Hovaquick into the Tekran sample probe loop upstream of the inertial filter. The loop flow rate was 53.5 lpm, which is the normal sampling flow rate. The flow rate of the oxidized calibration gas was ~10% of the total sample probe loop flow rate, and the concentration of the oxidized calibration was high enough to elevate the expected measured Hg concentration to between 1.8 and 2.0 times the native concentration. We defined the native concentration as the last observed (i.e., batch sample result) from the Tekran prior to injecting the oxidized calibration gas. The calibration gas was allowed to flow for a period of between 3 and 5 batch cycles, before cutting off the oxidized calibration gas flow in order to measure only stack Hg concentrations. The dynamic spike value was chosen from among the 3 to 5 measured spiked results that met the

dynamic spike performance criteria. The performance criteria for the pre-test dynamic spike are a recovery of 100±5% or an absolute difference of less than 0.2 µg/scm. In addition, the relative standard deviation of the three spike tests must be less than or equal to 5% or an average absolute difference of the three spikes less than or equal to 0.2 µg/scm. Tables 4 and 5 provide a summary of the dynamic spike results performed on August 29th.

Table 4: Summary of Practice Dynamic Spike Check – August 29, 2006

Pre-Test ID	Probe Flow Rate (lpm@20C)	Spike Flow Rate (lpm@20C)	Dilution Factor	Pre-Stack Concentration (ug/m^3)	Spike Solution Concentration (ug/m^3)	Target Spike Concentration (ug/m^3)	Actual Spike Concentration (ug/m^3)	Recovery (%)	Dynamic Spike Status
HS-Pre-1	53.50	5.35	10.00	0.53	5.1	0.99	0.99	101%	PASS
HS-Pre-2	53.50	5.25	10.19	0.42	4.3	0.80	0.79	97%	PASS
HS-Pre-3	53.50	5.26	10.17	0.41	4.3	0.79	0.78	97%	PASS
High Spike Avg.							Relative Standard Deviation:	2%	PASS

Table 5: Raw Data of Practice Dynamic Spike Check – August 29, 2006

Time	Condition	Concentration
8/29/2006 15:32	Native	0.61
8/29/2006 15:35	Native	0.57
8/29/2006 15:37	Native	0.54
8/29/2006 15:40	Native	0.53
8/29/2006 15:42	Native	0.56
8/29/2006 15:45	Native	0.53
8/29/2006 15:47	Target_1_0	0.46
8/29/2006 15:50	Target_1_0	0.35
8/29/2006 15:52	BlowbackFilter	0.69
8/29/2006 15:55	BlowbackLoop	0.85
8/29/2006 15:57	Continuous	0.99
8/29/2006 16:00	Target_1_0	0.99
8/29/2006 16:02	Target_1_0	1.01
8/29/2006 16:05	Native	0.99
8/29/2006 16:07	Native	0.48
8/29/2006 16:10	Native	0.42
8/29/2006 16:12	Target_0_8	0.45
8/29/2006 16:15	Target_0_8	0.79
8/29/2006 16:17	Target_0_8	0.87
8/29/2006 16:20	Target_0_8	0.79
8/29/2006 16:22	Native	0.87
8/29/2006 16:25	Native	0.42
8/29/2006 16:27	Native	0.43
8/29/2006 16:30	Native	0.41
8/29/2006 16:32	Target_0_8	0.77
8/29/2006 16:35	Target_0_8	0.78
8/29/2006 16:37	Target_0_8	0.84
8/29/2006 16:40	Native	0.97
8/29/2006 16:42	Native	1.08
8/29/2006 16:45	Native	0.91

The unit came back online early in the morning of August 30th.

August 30, 2006

Upon arrival at the plant site on the morning of August 30th, the unit was just starting to come up on load, and the mercury concentrations went from ~1.0 to 8.0 µg/scm. During the early phase of the unit start-up, the initial calibration of the Tekran was again checked. Based on the check of the calibration with elemental calibration gas, another elemental calibration error adjustment was repeated using the same procedures as detailed on August 28th. Another 3-level oxidized Hg calibration error test was also performed. Table 6 provides the results of both the elemental and oxidized checks.

Table 6: Summary of Elemental & Oxidized Hg Calibration Error Check – August 30th

Elemental Hg Calibration Error Check						
Calibration Gas Level	Reference Value (ug/m^3)	Verification Gas Level	Analyzer Response (ug/m^3)	Difference (ug/m^3)	Cal Error % of Span (%)	Cal Error Status
Low	2.52	LOW	2.56	0.0	0.4%	PASS
Mid	5.03	MID	5.08	0.0	0.5%	PASS
High	10.00		10.09	0.1	0.9%	PASS
Oxidized Hg Calibration Error Check						
Calibration Gas Level	Reference Value (ug/m^3)	Verification Gas Level	Analyzer Response (ug/m^3)	Difference (ug/m^3)	Cal Error % of Span (%)	Cal Error Status
Low	1.66	LOW	1.64	0.0	-0.2%	PASS
Mid	5.26	MID	4.88	-0.4	-3.8%	PASS
High	9.20		8.74	-0.5	-4.6%	PASS

After completion of the elemental calibration error check and the oxidized system integrity check, an attempt was made to perform the pre-test low-level dynamic spike. Due to the relatively high Hg concentration in the stack effluent (the selective catalytic reduction (SCR) had not been enabled), the target values of the low-level dynamic spike were above the defined IRM calibration span. The target value of the low-level dynamic spikes must be within 1.4 and 1.6 times the native stack concentration. An initial attempt was made to perform the low-level dynamic spike, but the native concentrations increased from ~2.7 µg/scm to 7.4 µg/scm over the course of a two-hour period. A total of four (4) low-level dynamic spikes were performed over a time period of 90 minutes. One of the four attempts was aborted due to changes in the native concentration. Table 7 provides a summary of the low-level dynamic spike results.

Table 7: Summary of Pre-Test Low-Level Dynamic Spike Results – August 30th

Pre-Test ID	Probe Flow Rate (lpm@20C)	Spike Flow Rate (lpm@20C)	Dilution Factor	Pre-Stack Concentration (ug/m^3)	Spike Solution Concentration (ug/m^3)	Target Spike Concentration (ug/m^3)	Actual Spike Concentration (ug/m^3)	Recovery (%)	Dynamic Spike Status
LS-Pre-1	53.50	6.10	8.77	7.62	36.9	10.96	10.77	96%	PASS
LS-Pre-2	53.50	6.10	8.77	6.95	36.9	10.37	10.20	96%	PASS
LS-Pre-3	53.50	6.10	8.77	6.35	36.5	9.79	9.90	103%	PASS
Low Spike Avg.						Relative Standard Deviation:		4%	PASS

Due to the relatively high native concentrations (i.e., ~7 to 8 µg/scm), a new oxidized standard was made in order to increase the spike concentration to 1.8 to 2.0 times the native concentration. A typical solution used to perform the system integrity checks is a mercuric chloride ($HgCl_2$) standard solution containing 10 milliliters (ml) of 9.95 ppm $HgCl_2$ diluted to 1000 ml. The high-level spike solution required 50 ml of standard

solution. The high-level dynamic spike experiment was performed over a time period of 150 minutes with a total of four (4) attempts made to achieve three successful dynamic spike results. The high dynamic spike attempts were complicated by the failure of the Hovaquick system to produce a consistent liquid $HgCl_2$ solution flow rate. It is crucial that the Hovaquick be able to give reproducible solution flow rates once the system is set up. The peristaltic pump for the liquid solution was not producing proper or reproducible flow rates during the third high-level dynamic spike attempt. It took approximately 60 minutes to get the adjustment on the peristaltic pump tubing set at the right tension to produce stable liquid solution flow rates. As with the low-level dynamic spike target values, the high-level target values were above the system's calibrated span. Table 8 provides a summary of the high-level dynamic spike results.

Table 8: Summary of Pre-Test High-Level Dynamic Spike Results – August 30th

Pre-Test ID	Probe Flow Rate (lpm@20C)	Spike Flow Rate (lpm@20C)	Dilution Factor	Pre-Stack Concentration (ug/m^3)	Spike Solution Concentration (ug/m^3)	Target Spike Concentration (ug/m^3)	Actual Spike Concentration (ug/m^3)	Recovery (%)	Dynamic Spike Status
HS-Pre-1	53.50	7.09	7.55	9.02	68.3	16.87	16.76	99%	PASS
HS-Pre-2	53.50	7.08	7.56	8.88	67.9	16.69	16.93	103%	PASS
HS-Pre-3	53.50	7.00	7.64	8.34	64.3	15.66	15.65	100%	PASS
High Spike Avg.						Relative Standard Deviation:		2%	PASS

Closing Comments

This was the first of a series of tests planned to evaluate the dynamic spiking procedures contained in the draft conceptual IRM. As can be seen from the results in the above discussion, the dynamic spike procedures can be done and produce what appear to be passing results. To be honest, the spike calibration gas was injected to the probe until an acceptable spike was measured. These dynamic spike tests were performed with the mindset of a stack tester trying to get the testing started and/or completed and, even with that perspective, were very time consuming. Additional testing will be done to evaluate the "stable response" criteria and other analyzers.

The only conclusions the dynamic spike testing revealed are that the procedure can be done, the system can read an elevated concentration and with some luck the measured values will be within 5% of the target value. Obviously, this is made easier if the native stack concentration does not change during a spiking attempt. There was no evidence of measurement or spectral interference revealed by the spiking procedure (at least on the Tekran system) so it does not appear to provide any additional QA/QC beyond the elemental and oxidized calibration error tests.

One main observation during this set of tests is that the Hg systems are not necessarily stable from day to day. Therefore, the initial 3-level elemental Hg calibration error and/or oxidized system integrity checks may need to be performed each day. Previous assumptions or performances of the IRM only performed those initial 3-level checks at the beginning of the test period. Conducting these initial calibrations every day will add approximately 2 hours per day during a RATA.

We do not believe that both elemental and oxidized are necessary on subsequent test days. Therefore, it should be possible to reduce these calibration error tests to just those

necessary to perform a good system calibration. Further experiments should provide additional guidance.

A second observation is that the system span needs to be at least 2.5 to 3.0 times the high end of the expected stack concentration. This is the only way to ensure that the target values during the high-level dynamic spike do not exceed the system span. This could effectively put a significant portion of the reference measurements in the lower 20% of the effective analyzer span.

Finally, the precision implied by the IRM calibration and spiking specifications forces the tester to take readings and perform calculations to the nearest 0.01 µg/scm. We do not believe that the systems can accurately measure 0.01 µg/scm, even on a short-term differential basis. On an absolute basis, we do not believe that 0.1 µg/scm can be accurately resolved but that level is certainly achievable on a differential basis. You will note that all of the tables in this report contain readings to two decimals but all results are only reported to one decimal.