MERCURY CEM CALIBRATION

TOPICAL REPORT

BY

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EXECUTIVE SUMMARY

Mercury continuous emissions monitoring systems (CEMS) are being implemented in over 800 coal-fired power plant stacks. The power industry desires to conduct at least a full year of monitoring before the formal monitoring and reporting requirement begins on January 1, 2009. It is important for the industry to have available reliable, turnkey equipment from CEM vendors. Western Research Institute (WRI) is working closely with the Electric Power Research Institute (EPRI), the National Institute of Standards and Technology (NIST), and the Environmental Protection Agency (EPA) to facilitate the development of the experimental criteria for a NIST traceability protocol for dynamic elemental mercury vapor generators. The generators are used to calibrate mercury CEMs at power plant sites. The Clean Air Mercury Rule (CAMR) which was published in the Federal Register on May 18, 2005 requires that calibration be performed with NIST-traceable standards (Federal Register 2007). Traceability procedures will be defined by EPA. An initial draft traceability protocol was issued by EPA in May 2007 for comment. In August 2007, EPA issued an interim traceability protocol for elemental mercury generators (EPA 2007). The protocol is based on the actual analysis of the output of each calibration unit at several concentration levels ranging initially from about 2-40 $\mu\text{g}/\text{m}^3$ elemental mercury, and in the future down to 0.2 $\mu\text{g}/\text{m}^3$, and this analysis will be directly traceable to analyses by NIST. The document is divided into two separate sections. The first deals with the qualification of generators by the vendors for use in mercury CEM calibration. The second describes the procedure that the vendors must use to certify the generator models that meet the qualification specifications. The NIST traceable certification is performance based,

traceable to analysis using isotope dilution inductively coupled plasma / mass spectrometry performed by NIST in Gaithersburg, MD. The outputs of mercury generators are compared to one another using a nesting procedure which allows direct comparison of one generator with another and eliminates analyzer variability effects.

The qualification portion of the EPA interim traceability protocol requires the vendors to define generator performance as affected by variables such as pressure, temperature, line voltage, and shipping. WRI is focusing efforts to determine actual generator performance related to the variables defined in the qualification portion of the interim protocol. The protocol will then be further revised by EPA based on what can actually be achieved with the generators. Another focus of the study is to evaluate approaches for field verification of generator performance. Upcoming work includes evaluation of oxidized mercury calibration generators, for which a separate protocol will be prepared by EPA. In addition, the variability of the spectrometers/analyzers under various environmental conditions needs to be defined and understood better.

The key results of experimental work performed by WRI in 2007 and early 2008 related to the draft qualification criteria and actual performance of generators are summarized below.

1. The output of the generators is highly linear.
2. Identical model elemental mercury generator units from the same vendor do not necessarily provide identical concentration outputs at the same settings. It must be assumed that each one is unique relative to its linear calibration equation or individual monitoring points (for single point calibration).
3. The effect of back pressure that can be encountered due to long stack umbilicals, up to 9 psi, is relatively minor. Each vendor deals with back pressure differently.
4. The effect of external pressure is relatively minor.
5. The effect of temperature is significant. Components of the generators such as Peltier coolers and mass flow controllers can be adversely affected by temperatures ranging from 10 to 30 °C. Therefore the units should be operated in environments as close to 20 °C as possible.
6. The effect of line voltage between 105 – 125 V depends on the specification of the OEM power supplies selected by the vendors for use in their equipment. Some units are affected, others are not.
7. Limited experience with shipping elemental generator units has indicated that this could be an issue of significant concern. Experimental procedures should be implemented to document that generator output has not changed during shipping. Possibly generators should be certified at the locations where they will be used.

8. The qualification test criteria to be established by EPA can be designed to be relatively simple, using a series of 3x3 matrixes (3 concentrations, 3 variable conditions) for each test. Candidate procedures were developed and demonstrated in the current study. Generator output was evaluated using three concentration settings: 5, 15, and 30 $\mu\text{g}/\text{m}^3$. Variables tested included back pressure, external pressure, external temperature, and line voltage. Each of these variables was tested by using no more than three conditions. For back pressure, this was no pressure applied, and line restrictions corresponding to 5 psi and 9 psi. For external pressure, output was evaluated at 0.78 atm. (barometric pressure of Laramie, WY), 0.95 atm, and 1.1 atm. The temperatures that were evaluated were 10, 20, and 30 °C. The line voltages that were tested were 105, 115, and 125 volts.
9. Analyzer stability and calibration drift over time needs to be studied further.
10. Possible approaches for verifying generator performance in the field could include measurement of output by a portable analyzer, collection of calibration gas from a generator using a sorbent tube followed by analysis of the tube, or nesting analysis against a certified calibration gas cylinder or reference generator.
11. Oxidized mercury calibration systems will need to be evaluated and procedures for ensuring NIST traceability will need to be evaluated and developed.
12. The test procedures used for evaluating the effects of the variables described in the Qualification Experiments section of this report provide real-world results that can be used in the future design and implementation of EPA-defined qualification test procedures.

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OBJECTIVES

A main objective of the current work is to provide data on the performance and capabilities of elemental mercury generator/calibration systems for the development of realistic NIST traceability protocols for mercury vapor standards for continuous emission CEM calibration. This work is providing a direct contribution to the enablement of continuous emissions monitoring at coal-fired power plants in conformance with the CAMR. EPA Specification 12 states that mercury CEMs must be calibrated with NIST-traceable standards (Federal Register 2005). The initial draft of an elemental mercury generator traceability protocol was circulated by EPA in May 2007 for comment, and an interim protocol was issued in August 2007 (EPA 2007). Initially it was assumed that the calibration and implementation of mercury CEMs would be relatively simple, and implementation would follow the implementation of the Clean Air Interstate Rule (CAIR) SO₂ and NO_x monitoring, and sulfur emissions cap and trade. However, mercury has proven to be significantly more difficult to accurately determine than was originally thought. The purpose of the current phase of this project is to evaluate issues related to the use of dynamic elemental mercury calibrators that are based on mercury vapor headspace above elemental mercury at a particular temperature.

INTRODUCTION

WRI is working closely with NIST and EPA to facilitate the development of a technically sound, yet practical traceability procedure that EPA can incorporate into a new traceability protocol. The WRI analytical group has unique specialized capabilities in analytical method development and validation that are being applied to this effort.

One goal of the project is to critically evaluate the performance capabilities of dynamic mercury vapor pressure generator technology for CEM calibration under a variety of conditions. This project involves the participation of CEM calibrator vendors to provide calibration equipment to WRI for evaluation of the technology (Horiba, Mercury Instruments, Nippon, and Thermo Fisher). In addition, a continuous atomic fluorescence analyzer was provided by Thermo Fisher, and a portable gold film resistance analyzer was provided by Arizona Instruments Co. The results and recommendations from the current phase of the effort are being provided to EPA and NIST on a continuous basis, and EPA is considering this information for future iterations of the traceability protocol for elemental mercury calibration using dynamic generators. WRI has no vested interest in the calibration or analysis technology from any vendor. It is not the intent of this study to rank units from various vendors or recommend units from one vendor over another. It is assumed that the vendors will continuously improve their platforms and products as this technology is implemented. The primary purpose of this study is to evaluate the technical potential of the technology in general, and assist EPA and NIST in providing the necessary protocols to allow its implementation for CEM calibration. A separate but related issue is that of oxidized mercury standards (Mercial, Hovacal, Thermo Fisher, others), which also will need to be addressed in the near future.

CEM Calibration and NIST Traceability

EPA Specification 12 which was issued on May 18, 2005, states that mercury CEMs must be calibrated with NIST-traceable standards (Federal Register 2005). The initial draft of an elemental mercury generator traceability protocol was circulated by EPA in May 2007 for comment, and an interim protocol was issued in August 2007 (EPA 2007). Initially it was assumed that the calibration and implementation of mercury CEMs would be relatively simple, and implementation would follow the implementation of the Clean Air Interstate Rule (CAIR) SO₂ and NO_x monitoring, and sulfur emissions cap and trade. However, mercury has proven to be significantly more difficult to accurately determine than was originally thought. The purpose of the current phase of this project is to evaluate issues related to the use of dynamic elemental mercury calibrators that are based on mercury vapor headspace above elemental mercury.

Calibration techniques for CEMs that have been proposed include calibration gas cylinders, mercury vapor permeation tubes, mercury diffusion tubes, and elemental vapor pressure generators. The latter technology is currently generating significant interest as the most viable approach for power plant deployment. This technology uses saturated headspace devices that contain a small amount of liquid elemental mercury in a temperature-controlled vessel, or equilibrium chamber. This technology has the possibility of generating large quantities of calibration gas over extended periods of time for CEM calibration. By precisely and accurately controlling and or measuring the equilibrium chamber temperature, a controlled concentration of mercury in nitrogen or air theoretically can be generated. Each vendor has developed a unique design for their elemental mercury generator unit. Typically, a low flow mass flow controller (cc/min) is used to sweep an equilibrium chamber. This is diluted further using a relatively high flow mass flow controller (L/min) to provide a diluted vapor calibration stream of known concentration. Several vendors are offering calibration devices based on this principle. These include Horiba, Mercury Instruments, Nippon, PSA, Tekran, and Thermo Fisher.

Prior Work

Prior to this project, NIST did not provide a recommended mercury vapor pressure equation or list mercury vapor pressure in its vapor pressure database. The NIST Physical and Chemical Properties Division in Boulder, Colorado was subcontracted under this project in 2005 to study the issue in detail and to recommend a mercury vapor pressure equation that the vendors of mercury vapor pressure calibration units can use to calculate the theoretical elemental mercury vapor concentration in an equilibrium chamber at a particular temperature. A NIST recommended equation was developed and published in the peer-reviewed literature as a result of this work (Huber et al. 2006). This equation is used to calculate the vapor pressure of liquid elemental mercury from the triple point to the boiling point, and provides a vapor pressure that is consistent with the Clausius/Clapeyron thermodynamic equation. The new NIST equation is different from some other equations in use, and it provides a vapor pressure at 20 °C about 7% higher than the mercury vapor pressure listed in the 1928 International Critical Tables. The new

NIST equation is cited as the basis for the mercury vapor pressure table in the 2007-2008 CRC Handbook of Chemistry and Physics (CRC 2007).

There continues to be disagreement among the vendors on the correct vapor pressure equation for use in the calibration units. Because of this, it was agreed in a special meeting held in Orlando, FL in March 16, 2006 that the NIST traceability of calibration units would be performance based. The issue of the correct vapor pressure equation is now a side issue, and this is no longer in the critical path for establishing a NIST traceability protocol. Also, work with units from the same vendor indicate the identical model units from the same vendor do not necessarily give identical elemental mercury output concentrations. In this circumstance, the use of a single equation for all units is of limited value (Schabron et al. 2007).

EXPERIMENTAL

Calibrators/generators were provided by four vendors. These included a Horiba ENDA-Hg 5000, a Mercury Instruments MC-3000, a Nippon Instruments Corporation MGS-1, and two Thermo Fisher Model 81i Mercury Calibrators. Manufacturer-prescribed operating instructions were followed for the use of each of these devices. The Horiba unit was an early prototype and it was not fully operational, therefore it was not include in the current study.

A Thermo Fisher Model 80i continuous emission atomic fluorescence elemental mercury analyzer was used as the primary analyzer for this study. The analyzer was not recalibrated prior to the start of the experiments described in this report. The analyzer was updated in April 2007 with the new Thermo iPort32 software with lamp heater upgrade kit provided by Thermo Fisher.

A Jerome Model J405 manufactured by Arizona Instrument LLC was evaluated as a possible portable analyzer to verify generator output. This analyzer is a portable unit weighing 5 pounds that uses gold film resistor sensor technology. The sensor was regenerated per the manufacturer's instructions prior to the start of each day of data collection. The unit was last calibrated at the factory in Tempe, AZ on April 30, 2007.

Two Thomas T-2820ST portable oil-free air compressors were used as the air source for the two Thermo 81i calibrators described in this report. The compressors replaced the use of compressed air cylinders. The compressor's air outlet was fitted with a regulator, an indicating desiccant chamber which functions as an air dryer, and a 5 micron particulate filter. The effect of the two air sources (cylinder vs. compressor) on manifold pressure and concentration using a Thermo Fisher 81i generator was evaluated experimentally and found to be insignificant. Breathing-quality compressed air cylinders were used as the air source for the Mercury Instruments MC-3000. Ultra high purity nitrogen cylinders were used as source gas for the Nippon and Horiba units.

INITIAL EXPERIMENTAL WORK

Nesting Analysis for Generator Comparison

Elemental Mercury Generators

Thermo 02 Model 81i Mercury Calibrator Serial Number 0613917136 was originally delivered to NIST in August 2006 and received at WRI in January 2007. Thermo 03 Model 81i Mercury Calibrator Serial Number 0636220561 was delivered to WRI in February 2007. Elemental mercury in the vapor outlet was measured with a Thermo Model 80i Mercury Analyzer Serial Number 0636220551 delivered to WRI in February 2007. Responses were recorded using a 60 second averaging time. Responses were recorded for 8 minute intervals after switching mercury generator sources, which included 3 minutes analyzer equilibration time prior to 5 minutes of data collection. When the mercury concentration was changed at the calibrator/generator, a minimum of 10 minutes equilibration time was allowed prior to the 5 minutes of data collection. Zero backgrounds at the analyzer were recorded at beginning and end of measurement sequences.

Mercury Vapor Introduction Device

A PFA “Tee” connector with compression fittings for ¼-inch outside diameter (O.D.) PFA tubing was employed as the initial design vapor introduction device for the 80i analyzer for the side by side nesting studies, including the nesting studies performed after one of the Thermo 81i units was later shipped and returned to WRI on two separate occasions. The configuration of the Tee is such that calibrator mercury vapor flow is delivered through one arm of the Tee perpendicular to the analyzer flow. A vacuum pump at the exit port of the 80i analyzer cell draws sample into the analyzer through the second arm of the Tee. The third arm of the Tee (180° opposite the analyzer flow) is vented to a negative pressure vent pipe arrangement via 6 feet of ¼-inch O.D. PFA tubing. Although this style of inlet has minimal void volume in the delivery of Mercury vapor to the analyzer, it is likely that the 6-foot length of vent tubing causes some back pressure at the analyzer inlet. For the initial nesting studies comparing two identical model numbers, this was not problematic since tubing lengths and flow rates were kept consistent for identical generator concentration settings.

Nesting Results

Results from a series of intra-day and inter-day data obtained using a nesting procedure provided by Bill Dorko at NIST in Gaithersburg, MD are provided in Table 1. The response values for each of the seven data sets are five minute average responses of the two Thermo 81i generators compared to each other at four concentrations ranging from 5-50 $\mu\text{g}/\text{m}^3$ over 5 days. The “Day 1 Results” “Day 2 Results” etc. are nesting ratios of the responses as indicated by the formula. The responses and nesting ratios are diagnostic of analyzer drift and/or calibrator drift. A changing ratio indicates relative output differences between the calibrators. Analyzer drift would be reflected as absolute response values that change while the ratios remain essentially constant.

Table 1. Nesting Data for Two Thermo 81i Generators Over a Five-Day Period

Day 1—04/30/2007—Monday Reference: WRI Notebook 1190 Page 35 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>				Day 2—05/01/2007—Tuesday Reference: WRI Notebook 1190 Page 36 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>				Day 3—05/02/2007—Wednesday Reference: WRI Notebook 1190 Page 36 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>			
<i>5 µg/m³ Nominal</i>	<i>Hg⁰ µg/m³</i>	<i>Nesting Ratio</i>	Day 1 Results	<i>5 µg/m³ Nominal</i>	<i>Hg⁰ µg/m³</i>	<i>Nesting Ratio</i>	Day 2 Results	<i>5 µg/m³ Nominal</i>	<i>Hg⁰ µg/m³</i>	<i>Nesting Ratio</i>	Day 3 Results
Thermo02 Res1	4.90401			Thermo02 Res1	4.64911			Thermo02 Res1	4.86977		
Thermo03 Res2	4.70162	Res2/Avg(Res1,3)	0.958846	Thermo03 Res2	4.40678	Res2/Avg(Res1,3)	0.948308	Thermo03 Res2	4.62303	Res2/Avg(Res1,3)	0.953583
Thermo02 Res3	4.90282			Thermo02 Res3	4.64487			Thermo02 Res3	4.82636		
Thermo03 Res4	4.68217	Res4/Avg(Res3,5)	0.954739	Thermo03 Res4	4.39951	Res4/Avg(Res3,5)	0.947230	Thermo03 Res4	4.60865	Res4/Avg(Res3,5)	0.954613
Thermo02 Res5	4.90545			Thermo02 Res5	4.64434			Thermo02 Res5	4.82918		
Thermo03 Res6	4.68038	Res6/Avg(Res5,7)	0.954334	Thermo03 Res6	4.36463	Res6/Avg(Res5,7)	0.943736	Thermo03 Res6	4.59895	Res6/Avg(Res5,7)	0.953921
Thermo02 Res7	4.90323			Thermo02 Res7	4.60534			Thermo02 Res7	4.81302		
<i>15 µg/m³ Nominal</i>				<i>15 µg/m³ Nominal</i>				<i>15 µg/m³ Nominal</i>			
Thermo02 Res1	14.5622			Thermo02 Res1	13.6579			Thermo02 Res1	14.2247		
Thermo03 Res2	14.6598	Res2/Avg(Res1,3)	1.00724	Thermo03 Res2	13.7563	Res2/Avg(Res1,3)	1.00746	Thermo03 Res2	14.3515	Res2/Avg(Res1,3)	1.00857
Thermo02 Res3	14.5467			Thermo02 Res3	13.6511			Thermo02 Res3	14.2345		
Thermo03 Res4	14.6636	Res4/Avg(Res3,5)	1.00801	Thermo03 Res4	13.7345	Res4/Avg(Res3,5)	1.00625	Thermo03 Res4	14.3565	Res4/Avg(Res3,5)	1.00852
Thermo02 Res5	14.5474			Thermo02 Res5	13.6473			Thermo02 Res5	14.2359		
Thermo03 Res6	14.6480	Res6/Avg(Res5,7)	1.00758	Thermo03 Res6	13.7290	Res6/Avg(Res5,7)	1.00662	Thermo03 Res6	14.3377	Res6/Avg(Res5,7)	1.00791
Thermo02 Res7	14.5283			Thermo02 Res7	13.6300			Thermo02 Res7	14.2145		
<i>30 µg/m³ Nominal</i>				<i>30 µg/m³ Nominal</i>				<i>30 µg/m³ Nominal</i>			
Thermo02 Res1	28.5773			Thermo02 Res1	26.8947			Thermo02 Res1	28.0076		
Thermo03 Res2	29.5919	Res2/Avg(Res1,3)	1.03617	Thermo03 Res2	27.9215	Res2/Avg(Res1,3)	1.03830	Thermo03 Res2	29.0563	Res2/Avg(Res1,3)	1.03802
Thermo02 Res3	28.5407			Thermo02 Res3	26.8885			Thermo02 Res3	27.9763		
Thermo03 Res4	29.5723	Res4/Avg(Res3,5)	1.03614	Thermo03 Res4	27.9081	Res4/Avg(Res3,5)	1.03806	Thermo03 Res4	29.0115	Res4/Avg(Res3,5)	1.03743
Thermo02 Res5	28.5409			Thermo02 Res5	26.8814			Thermo02 Res5	27.9534		
Thermo03 Res6	29.5638	Res6/Avg(Res5,7)	1.03724	Thermo03 Res6	27.9114	Res6/Avg(Res5,7)	1.03825	Thermo03 Res6	29.0022	Res6/Avg(Res5,7)	1.03781
Thermo02 Res7	28.4640			Thermo02 Res7	26.8849			Thermo02 Res7	27.9378		
<i>50 µg/m³ Nominal</i>				<i>50 µg/m³ Nominal</i>				<i>50 µg/m³ Nominal</i>			
Thermo02 Res1	46.5299			Thermo02 Res1	44.3212			Thermo02 Res1	45.9896		
Thermo03 Res2	49.1648	Res2/Avg(Res1,3)	1.05799	Thermo03 Res2	46.7071	Res2/Avg(Res1,3)	1.05451	Thermo03 Res2	48.4977	Res2/Avg(Res1,3)	1.05524
Thermo02 Res3	46.4102			Thermo02 Res3	44.2638			Thermo02 Res3	45.9279		
Thermo03 Res4	49.1132	Res4/Avg(Res3,5)	1.05924	Thermo03 Res4	46.6228	Res4/Avg(Res3,5)	1.05458	Thermo03 Res4	48.4875	Res4/Avg(Res3,5)	1.05635
Thermo02 Res5	46.3231			Thermo02 Res5	44.1561			Thermo02 Res5	45.8739		
Thermo03 Res6	49.0407	Res6/Avg(Res5,7)	1.06046	Thermo03 Res6	46.5877	Res6/Avg(Res5,7)	1.05525	Thermo03 Res6	48.4684	Res6/Avg(Res5,7)	1.05781
Thermo02 Res7	46.1662			Thermo02 Res7	44.1406			Thermo02 Res7	45.7656		
<i>Hg⁰ Background -0.0459616 µg/m³ at end of sequence</i>				<i>Hg⁰ Background -0.0319050 µg/m³ at end of sequence</i>				<i>Hg⁰ Background -0.0260793 µg/m³ at end of sequence</i>			

Table 1. Nesting Data for Two Thermo 81i Generators Over a Five-Day Period (con't)

Day 4—05/03/2007—Thursday Reference: WRI Notebook 1190 Page 36 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>				Day 5—05/04/2007—Friday Reference: WRI Notebook 1190 Page 36 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>			
<u>5 µg/m³ Nominal</u>	<u>Hg⁰ µg/m³</u>	<u>Nesting Ratio</u>	Day 4 Results	<u>5 µg/m³ Nominal</u>	<u>Hg⁰ µg/m³</u>	<u>Nesting Ratio</u>	Day 5 Results
Thermo02 Res1	5.05264			Thermo02 Res1	5.28258		
Thermo03 Res2	4.79054	Res2/Avg(Res1,3)	0.950732	Thermo03 Res2	5.12191	Res2/Avg(Res1,3)	0.97060
Thermo02 Res3	5.02494			Thermo02 Res3	5.27152		
Thermo03 Res4	4.76662	Res4/Avg(Res3,5)	0.950086	Thermo03 Res4	5.07669	Res4/Avg(Res3,5)	0.96294
Thermo02 Res5	5.00914			Thermo02 Res5	5.27261		
Thermo03 Res6	4.75800	Res6/Avg(Res5,7)	0.950435	Thermo03 Res6	5.07677	Res6/Avg(Res5,7)	0.96324
Thermo02 Res7	5.00312			Thermo02 Res7	5.26841		
<u>15 µg/m³ Nominal</u>				<u>15 µg/m³ Nominal</u>			
Thermo02 Res1	14.8061			Thermo02 Res1	15.5442		
Thermo03 Res2	14.9360	Res2/Avg(Res1,3)	1.00884	Thermo03 Res2	15.6902	Res2/Avg(Res1,3)	1.00946
Thermo02 Res3	14.8040			Thermo02 Res3	15.5420		
Thermo03 Res4	14.9436	Res4/Avg(Res3,5)	1.00929	Thermo03 Res4	15.6944	Res4/Avg(Res3,5)	1.00967
Thermo02 Res5	14.8082			Thermo02 Res5	15.5461		
Thermo03 Res6	14.9419	Res6/Avg(Res5,7)	1.00873	Thermo03 Res6	15.6896	Res6/Avg(Res5,7)	1.00933
Thermo02 Res7	14.8169			Thermo02 Res7	15.5430		
<u>30 µg/m³ Nominal</u>				<u>30 µg/m³ Nominal</u>			
Thermo02 Res1	29.1400			Thermo02 Res1	30.5813		
Thermo03 Res2	30.1571	Res2/Avg(Res1,3)	1.03552	Thermo03 Res2	31.6251	Res2/Avg(Res1,3)	1.03450
Thermo02 Res3	29.1056			Thermo02 Res3	30.5595		
Thermo03 Res4	30.1655	Res4/Avg(Res3,5)	1.03698	Thermo03 Res4	31.6140	Res4/Avg(Res3,5)	1.03476
Thermo02 Res5	29.0742			Thermo02 Res5	30.5445		
Thermo03 Res6	30.1336	Res6/Avg(Res5,7)	1.03700	Thermo03 Res6	31.6078	Res6/Avg(Res5,7)	1.03504
Thermo02 Res7	29.0428			Thermo02 Res7	30.5312		
<u>50 µg/m³ Nominal</u>				<u>50 µg/m³ Nominal</u>			
Thermo02 Res1	47.5320			Thermo02 Res1	49.6010		
Thermo03 Res2	50.2901	Res2/Avg(Res1,3)	1.05936	Thermo03 Res2	52.6691	Res2/Avg(Res1,3)	1.06542
Thermo02 Res3	47.4126			Thermo02 Res3	49.2694		
Thermo03 Res4	50.2233	Res4/Avg(Res3,5)	1.06086	Thermo03 Res4	52.6159	Res4/Avg(Res3,5)	1.07391
Thermo02 Res5	47.2713			Thermo02 Res5	48.7200		
Thermo03 Res6	50.1534	Res6/Avg(Res5,7)	1.06276	Thermo03 Res6	52.3867	Res6/Avg(Res5,7)	1.08004
Thermo02 Res7	47.1124			Thermo02 Res7	48.2890		
<i>Hg⁰ Background -0.0101699 µg/m³ at end of sequence</i>				<i>Hg⁰ Background 0.00645250 µg/m³ at end of sequence</i>			

The results show that two generators of the same model and manufacturer do not exhibit identical concentrations at identical settings. Their relative outputs remain constant throughout the initial five-day nesting study with repeated measurements. This is illustrated by plotting one set of nesting ratios between the two generators at settings of 30 µg/m³ (Figure 1).

Figure 1. Nesting Ratio Plot for 30 µg/m³ Set Point Concentration for Two Thermo 81i Units

The Effect of Shipping

The generator designated Thermo 02 was shipped to NIST for certification as a Vendor Prime reference unit. However, NIST notified WRI that they suspected that the unit had changed due to shipping. It was returned to WRI in August 2007, and the nesting study was repeated. The results are provided in Table 2. On comparison with Thermo 03, the shipped Thermo 02 unit mercury concentration output had decreased significantly (Table 2, Day 6). This was greater than a 30% drop at 30 µg/m³ compared to the initial nesting study (Table 2, Day 5).

Table 2. Nesting Study Results Before and After Shipping Thermo 81i - 02 Unit Twice

Day 5—05/04/2007—Friday Reference: WRI Notebook 1190 Page 36 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>				After Thermo02 Shipped To/From NIST—08/29/07 Reference: WRI Notebook 1190 Page 71 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>				After Thermo02 Shipped To/From Thermo—09/28/07 Reference: WRI Notebook 1190 Page 75-76 Note—Responses 1-7 below are 5 minute average values <i>Hg⁰ Background set to 0 µg/m³ Nominal at start of sequence</i>			
<i>5 µg/m³ Nominal</i>	<i>Hg⁰ µg/m³</i>	<i>Nesting Ratio</i>	Day 5 Results	<i>5 µg/m³ Nominal</i>	<i>Hg⁰ µg/m³</i>	<i>Nesting Ratio</i>	Day 6 Shipping Results	<i>5 µg/m³ Nominal</i>	<i>Hg⁰ µg/m³</i>	<i>Nesting Ratio</i>	Day 7 Shipping Results
Thermo02 Res1	5.28258			Thermo02 Res1	5.64683			Thermo02 Res1	5.70033		
Thermo03 Res2	5.12191	Res2/Avg(Res1,3)	0.97060	Thermo03 Res2	5.74599	Res2/Avg(Res1,3)	1.01649	Thermo03 Res2	5.75795	Res2/Avg(Res1,3)	1.01062
Thermo02 Res3	5.27152			Thermo02 Res3	5.65868			Thermo02 Res3	5.69461		
Thermo03 Res4	5.07669	Res4/Avg(Res3,5)	0.96294	Thermo03 Res4	5.71360	Res4/Avg(Res3,5)	1.01055	Thermo03 Res4	5.71182	Res4/Avg(Res3,5)	1.00357
Thermo02 Res5	5.27261			Thermo02 Res5	5.64926			Thermo02 Res5	5.68844		
Thermo03 Res6	5.07677	Res6/Avg(Res5,7)	0.96324	Thermo03 Res6	5.69785	Res6/Avg(Res5,7)	1.00905	Thermo03 Res6	5.68185	Res6/Avg(Res5,7)	1.00063
Thermo02 Res7	5.26841			Thermo02 Res7	5.64421			Thermo02 Res7	5.66806		
<i>15 µg/m³ Nominal</i>				<i>15 µg/m³ Nominal</i>				<i>15 µg/m³ Nominal</i>			
Thermo02 Res1	15.5442			Thermo02 Res1	15.8719			Thermo02 Res1	16.5770		
Thermo03 Res2	15.6902	Res2/Avg(Res1,3)	1.00946	Thermo03 Res2	17.3116	Res2/Avg(Res1,3)	1.08446	Thermo03 Res2	17.1534	Res2/Avg(Res1,3)	1.03374
Thermo02 Res3	15.5420			Thermo02 Res3	16.0549			Thermo02 Res3	16.6100		
Thermo03 Res4	15.6944	Res4/Avg(Res3,5)	1.00967	Thermo03 Res4	17.2683	Res4/Avg(Res3,5)	1.07012	Thermo03 Res4	17.1843	Res4/Avg(Res3,5)	1.03416
Thermo02 Res5	15.5461			Thermo02 Res5	16.2187			Thermo02 Res5	16.6232		
Thermo03 Res6	15.6896	Res6/Avg(Res5,7)	1.00933	Thermo03 Res6	17.2150	Res6/Avg(Res5,7)	1.05618	Thermo03 Res6	17.1791	Res6/Avg(Res5,7)	1.03363
Thermo02 Res7	15.5430			Thermo02 Res7	16.3798			Thermo02 Res7	16.6172		
<i>30 µg/m³ Nominal</i>				<i>30 µg/m³ Nominal</i>				<i>30 µg/m³ Nominal</i>			
Thermo02 Res1	30.5813			Thermo02 Res1	28.3208			Thermo02 Res1	32.5170		
Thermo03 Res2	31.6251	Res2/Avg(Res1,3)	1.03450	Thermo03 Res2	34.4511	Res2/Avg(Res1,3)	1.20801	Thermo03 Res2	34.3123	Res2/Avg(Res1,3)	1.05544
Thermo02 Res3	30.5595			Thermo02 Res3	28.7169			Thermo02 Res3	32.5028		
Thermo03 Res4	31.6140	Res4/Avg(Res3,5)	1.03476	Thermo03 Res4	34.2933	Res4/Avg(Res3,5)	1.19125	Thermo03 Res4	34.2967	Res4/Avg(Res3,5)	1.05540
Thermo02 Res5	30.5445			Thermo02 Res5	28.8585			Thermo02 Res5	32.4903		
Thermo03 Res6	31.6078	Res6/Avg(Res5,7)	1.03504	Thermo03 Res6	34.1931	Res6/Avg(Res5,7)	1.18012	Thermo03 Res6	34.2971	Res6/Avg(Res5,7)	1.05555
Thermo02 Res7	30.5312			Thermo02 Res7	29.0902			Thermo02 Res7	32.4939		
<i>50 µg/m³ Nominal</i>				<i>50 µg/m³ Nominal</i>				<i>50 µg/m³ Nominal</i>			
Thermo02 Res1	49.6010			Thermo02 Res1	40.5767			Thermo02 Res1	53.2486		
Thermo03 Res2	52.6691	Res2/Avg(Res1,3)	1.06542	Thermo03 Res2	56.4233	Res2/Avg(Res1,3)	1.38732	Thermo03 Res2	56.7940	Res2/Avg(Res1,3)	1.06696
Thermo02 Res3	49.2694			Thermo02 Res3	40.7650			Thermo02 Res3	53.2113		
Thermo03 Res4	52.6159	Res4/Avg(Res3,5)	1.07391	Thermo03 Res4	56.3061	Res4/Avg(Res3,5)	1.37727	Thermo03 Res4	56.7317	Res4/Avg(Res3,5)	1.06684
Thermo02 Res5	48.7200			Thermo02 Res5	40.9996			Thermo02 Res5	53.1438		
Thermo03 Res6	52.3867	Res6/Avg(Res5,7)	1.08004	Thermo03 Res6	56.1833	Res6/Avg(Res5,7)	1.35630	Thermo03 Res6	56.6577	Res6/Avg(Res5,7)	1.06674
Thermo02 Res7	48.2890			Thermo02 Res7	41.8486			Thermo02 Res7	53.0825		
<i>Hg⁰ Background 0.00645250 µg/m³ at end of sequence</i>				<i>Hg⁰ Background -0.0276982 µg/m³ at end of sequence</i>				<i>Hg⁰ Background -0.00672761 µg/m³ at end of sequence</i>			

The Thermo 02 generator unit was shipped back to Thermo Fisher for repair. On receipt by Thermo Fisher, they examined it and noted that it appeared to be operating normally. Thermo Fisher returned it to WRI in September 2007, whereupon the nesting study was repeated again (Table 2, Day 7). Indeed, the unit was behaving much closer to what it was doing initially. However it was still slightly different than it was in the first nesting study. The changes are illustrated in a series of plots in Figure 2. The nesting results showed that the concentration output of the generator changed each time it was shipped. The exact cause of this remains unknown. Possibly the packing in the molecular sieve bed containing the elemental mercury was shifted during shipping, causing a transient bypass air channel for the air flow through the equilibrium chamber. Upon further shipping, the bed possibly settled back to its original configuration.

Figure 2. Changes in Output Concentration Due to Two Shipping Events (Day 6, Day 7)

Although this limited experience might not be representative of all units, a caution flag should be raised about shipping generator units. This could become an item of major concern in how the traceability protocol is written. Possibly certification should be conducted or verified at the site where the units will be used. Procedures such as the use of a stable pre-calibrated

analyzer, carbon tube sampling, or nesting analysis against certified gas cylinders or a reference generator may need to be considered.

In addition, two of the vendor calibrator units, Horiba and Nippon, require that portions of liquid elemental mercury be removed prior to shipment and added again by the receiving party. The mercury added will usually be from a different batch or source than that removed at the shipping location. This means that by definition, each time the unit is shipped it has been altered. The Mercury Instruments unit contains a liquid pool of mercury in the equilibrium chamber. In its original configuration, the vendor specified that it must not be tipped over during shipping. However, the compartment design has since been modified by the vendor to allow tipping, which is likely to occur during shipping.

Two Generator Platforms

During the course of this study, it became apparent that there are two types of platform designs for elemental mercury generators. Some units provide constant vapor part-per-billion (vppb) output, and others provide constant $\mu\text{g}/\text{m}^3$ output. This is important information if the outputs of different generators and analyzers are to be compared nose-to-nose at elevations other than sea level (1.0 atm.). Gas cylinders provide a constant vppb output. The Tekran and Thermo generators also provide a constant vppb output. These units have internal back pressure transducers, and the molar air flow from either the equilibrium chamber mass flow controller (Tekran) or the dilution mass flow controller (Thermo) is constantly adjusted to provide a constant vppb output regardless of elevation or back pressure. The Horiba, Mercury Instruments, and Nippon units, however, do not employ this feature. They provide constant $\mu\text{g}/\text{m}^3$ output regardless of elevation and back pressure. The significance is illustrated in a calculated example in Table 3 for the different types of platforms for nominal generator settings of $5 \mu\text{g}/\text{m}^3$.

Table 3. Actual Concentration Output for Two Types of Generator Platforms at 20°C

Calibrator Unit	Elevation, feet	P, atm	$\mu\text{g}/\text{m}^3$	vppb
Gas Cylinder, Thermo 81i, and Tekran 3310	0 (Sea Level)	1.0	5.0	0.60
	7,200	0.78	3.9	0.60
Horiba ENDA-Hg5000, Mercury Instruments MC-3000, and Nippon MGS-1	0 (Sea Level)	1.0	5.0	0.60
	7,200	0.78	5.0	0.77

When set at 5 $\mu\text{g}/\text{m}^3$, the output of the Thermo 81i generator corresponds to the vppb value that corresponds to 5 $\mu\text{g}/\text{m}^3$ at standard conditions (1.0 atm, 20 °C), or 0.60 vppb. This is compatible with the Thermo 80i analyzer, which is a continuous atomic fluorescence device in which the sample is drawn into a reduced pressure optical chamber. As long as the pressure within the optical chamber is constant for a series of measurements, the instrument is actually measuring vppb (number of molecules of mercury per number of molecules of air plus mercury). However, the readout concentration of the 80i analyzer is presented in units of $\mu\text{g}/\text{m}^3$ at standard conditions (1.0 atm, 20 °C).

Pressure and Temperature Manifold Analyzer Inlet

An inlet manifold was initially constructed at WRI to allow the comparison of various generators and analyzers using different platforms for experiments related to the elemental mercury calibrator traceability protocol. For the Tee used in head-to head comparison in the initial nesting analysis, measurement of the temperature and pressure is not important since the flow from both generators was identical at the same concentration settings. However, the various generators for comparison in subsequent experiments did not have identical flow settings under various conditions of comparison. The inlet manifold was also designed to allow for comparisons of two different analyzers using a single mercury generator.

A custom jar-style gas sampling manifold was fabricated from a 250-mL amber glass jar with PTFE-lined lid. This provides an elemental mercury vapor introduction device for the analyzer(s) that allow measurement of both temperature and pressure just before the analyzer inlet. Using the manifold, elemental mercury vppb and $\mu\text{g}/\text{m}^3$ conversion calculations are possible between the different platforms using the actual values of temperature and pressure. A diagram of the manifold is shown in Figure 3. A photograph of the manifold set up for laboratory use is attached as Figure 4. The manifold has six 1/4-inch PFA ports that are installed through the PTFE-lined jar lid.

Figure 3. Diagram of Jar-Style Gas Sampling Manifold

Figure 4. Manifold Installed for Laboratory Work

Port 1 is the mercury calibration gas vapor flow delivered by the calibrator into the manifold. Inside the jar, the section of PFA tubing for Port 1 extends to within $\frac{1}{4}$ -inch of the jar bottom. This is the longest section of tubing inside the jar of all six ports. Outside the jar, the PFA tubing ends in a PFA union 12 inches above the jar lid. This union facilitates quick and easy tubing connect/disconnect for the various generator changes. Port 1 in the photo is the front left port. The connect/disconnect union was added after the photo was taken, when it was apparent that generator/calibrator changes needed to occur more quickly and efficiently than could be performed at the jar union.

In Figure 4, Port 2 is the mercury vapor sampling outlet to a portable Jerome J405 mercury analyzer. Inside the jar, the section of PFA tubing extends to the middle of the jar. Ports 2, 3, 5, and 6 have equal lengths of tubing that extend to the middle of the jar (see Figure 3). Outside the jar, there is a 36-inch section of tubing that extends to the J405 or other analyzer inlet. The J405 analyzer is the yellow device behind the jar manifold in the photo. Port 3 is for

the digital pressure indicator. Above the jar lid, a 3/4-inch length section of 1/4-inch O.D. Viton tubing connects the jar union to the digital pressure indicator. In the photo, the indicator is the blue device connected to Port 3 by the short length of black Viton tubing. The pressure readout was set to display units of mm Hg, pressure, which was then converted to atmospheres (atm).

Port 4 is the manifold atmospheric dump. This port is diametrically opposed to Port 1. Inside the jar, it has the shortest length of tubing. Above the jar lid, a 6-inch length of 1/4-inch O.D. PFA tubing is necessary for clearance, which is then clamped to a 1-inch O.D. section of Tygon tubing. The large diameter Tygon tubing is visible at the top of the photo. The Tygon tubing is subsequently vented using a negative pressure vent duct which is outside the left frame of the photo. It was later determined that a 3/8-inch dump vent is more ideal for eliminating pressure in the manifold due to the relatively high dilution mass flow controller flow rates required to achieve low generator concentration settings. A 3/8-inch vent setup was later adopted and used for the work described in the Qualification Experiments section of this report.

Port 5 is a PFA-coated 1/4-inch O.D. diameter thermocouple. It extends into the jar to the same length as Ports 2, 3, and 5. Port 5 is symmetrically opposed to the pressure indicator in Port 3. In the photo, the thermocouple and its digital temperature display are the black rod and black microprocessor to the right of the manifold.

Port 6 is the manifold flow outlet to the Thermo 80i analyzer. The outlet is a 3-foot section of PFA tubing to the back of the analyzer (visible in the upper right portion of Figure 4). Port 6 is symmetrically opposed to Port 2 (the Jerome analyzer) with equal lengths of tubing for each analyzer. An external vacuum pump pulls manifold vapor through the 80i. The vacuum pump in this setup is outside the right frame of Figure 4.

Manifold Part Numbers

Jar/Lid:	Fisher 12-100-164
Unions (7 total):	Swagelok PFA-420-6
PFA Tubing:	Swagelok PFA-T4-062-100
Digital Pressure:	Omega DPI705-030A
Thermocouple:	Omega ICSS-14G-12-PFA
Thermocouple Processor:	Omega HH22

Output Characteristics of Three Generators

Experiments were conducted to provide linearity data to determine an initial set of performance characteristics for three different-vendor elemental mercury calibrator units. These included the Thermo Electron Corp. 81i, Mercury Instruments MC-3000, and Nippon Instruments Corporation MGS-1.

The custom jar-style gas sampling manifold was used to provide an introduction device for the analyzer in which vapor temperature and pressure can be measured. The data presented below are not corrected for temperature and pressure readings from the manifold, which are provided for reference purposes only. The Thermo 80i spectrometer was not calibrated since a NIST-traceable elemental mercury vapor standard was not available.

Thermo 81i (Thermo 03) The results obtained for Thermo 03 are presented in Table 4.

Table 4. Thermo 81i - 03 Linearity Data Using Manifold

81i Setpoint	80i 5-min avg, µg/m3	Manifold T, °F	Manifold P, atm
3 µg/m3 nominal	3.57549	72.5	0.8111
5 µg/m3 nominal	5.92448	72.9	0.8013
10 µg/m3 nominal	11.7943	73.3	0.7939
15 µg/m3 nominal	17.6851	73.5	0.7914
20 µg/m3 nominal	23.6116	73.7	0.7904
30 µg/m3 nominal	35.4277	74.0	0.7889
40 µg/m3 nominal	47.2897	74.2	0.7884
50 µg/m3 nominal	59.2391	74.6	0.7882

Operation of the 81i requires that the user specify the desired mercury concentration, and the unit's algorithms choose the source and dilution flow rates. The flow rates in turn affected the spectrometer inlet manifold pressure (highlighted in yellow), and a total manifold pressure change of almost 3% (relative) over the range of settings was observed. Note that the three highest nominal settings use relatively low dilution flow rates that produce manifold pressures close to the ambient barometric pressure of Laramie, WY at an elevation of 7,200 ft.

A plot of the Thermo 03 nominal settings vs. the 80i 5-min average results is presented in Figure 5. The response profile is highly linear, with a slope of about 1.2.

Figure 5. Thermo 81i - 03 Linearity Plot Using Manifold

Mercury Instruments MC-3000 (Mercury Instruments 02) The results obtained for the Mercury Instruments 02 calibrator are presented in Table 5 below.

Table 5. Mercury Instruments MC-3000 Linearity Data Using Manifold

MC-3000 Nominal Setting	80i 5-min avg, $\mu\text{g}/\text{m}^3$	Manifold T, $^{\circ}\text{F}$	Manifold P, atm
3.5 $\mu\text{g}/\text{m}^3$ (5.0 L/min)	6.32886	72.4	0.7780
10.0 $\mu\text{g}/\text{m}^3$ (5.0 L/min)	16.1678	72.4	0.7780
15.0 $\mu\text{g}/\text{m}^3$ (5.0 L/min)	23.6259	72.8	0.7780
30.0 $\mu\text{g}/\text{m}^3$ (2.5 L/min)	47.3777	73.2	0.7774
39.7 $\mu\text{g}/\text{m}^3$ (2.5 L/min)	62.6919	73.7	0.7772

Operation of the MC-3000 requires that the dilution flow be specified by the user. The dilution flows used for each of the settings are indicated in parentheses. The corresponding manifold pressure data (highlighted in yellow) are consistent with very low flow rates. In fact, the MC-3000 only delivers $\sim 40\%$ of the total flow indicated in parentheses through its mercury calibration gas vapor port, and as such, is delivering ~ 2.5 L/min and ~ 1.0 L/min, depending on the setting, to the manifold. The remaining flow is vented through a charcoal scrubber at the rear of the calibrator. A plot of the Mercury Instruments 02 nominal settings vs. the 80i 5-min average results is presented in Figure 6. The concentration profile at STP conditions is linear with a slope of about 1.6. The slope is higher than the slope for the Thermo 81i unit (Figure 3) because, as mentioned earlier, the MC-3000 is a constant $\mu\text{g}/\text{m}^3$ platform device, compared with the Thermo 81i, a constant vppb device. Also, the MC-3000 was used with the NIST Equation option, while the Thermo 81i was using the earlier equation to calculate mercury vapor pressure.

Figure 6. Mercury Instruments MC-3000 Linearity Plot Using Manifold

Nippon Instruments Corporation MGS-1 (Nippon 02) The results obtained for the Nippon 02 calibrator are presented in Table 6.

Table 6. Nippon MGS-1 Linearity Data Using Manifold

MGS-1 Nominal Setting	80i 5-min avg, $\mu\text{g}/\text{m}^3$	Manifold T, $^{\circ}\text{F}$	Manifold P, atm
3.7 $\mu\text{g}/\text{m}^3$ (0.25,10)	4.59432	76.8	0.7922
7.5 $\mu\text{g}/\text{m}^3$ (0.50,10)	8.54094	77.6	0.7922
11.2 $\mu\text{g}/\text{m}^3$ (0.75,10)	11.1817	78.2	0.7922
14.9 $\mu\text{g}/\text{m}^3$ (1.00,10)	12.5647	78.2	0.7922
29.8 $\mu\text{g}/\text{m}^3$ (1.00,5)	26.0826	77.9	0.7807
59.7 $\mu\text{g}/\text{m}^3$ (1.00,2.5)	77.0211	77.6	0.7774

Operation of the MGS-1 requires that both the source flow and the dilution flow be specified by the user. These are indicated in parentheses above; the first value is in units of mL/min, while the second value is in units of L/min. The two flow set points determine the resulting elemental mercury concentration. The pressure data (highlighted in yellow) are indicative of the three dilution air flows used for the range of settings chosen.

A plot of the Nippon 02 nominal settings vs. the 80i 5-min average results is presented in Figure 7.

Figure 7. Nippon MGS-1 Linearity Plot Using Manifold

The concentration profile is not very linear when compared with the profiles obtained for the other two calibrators. These experiments were performed using the Nippon generator without its optional booster pump that is typically placed between the generator and the probe umbilical to eliminate the effect of back pressure on the generator. Subsequent experiments

described in the Qualification Experiments section of this report show that the Nippon generator provides a linear output when the booster pump is used.

Back Pressure – Initial Studies

The effects of back pressure were initially evaluated in a series of experiments related to the elemental mercury traceability protocol. A range of flow restrictions and backpressures were applied to the vapor outlet ports of three elemental mercury calibrators/generators. These were intended to simulate a variety of field conditions where long lengths of tubing, such as those used for umbilical lines for CEM probes, may apply a backpressure as high as 0.6 atm (9 psi) to a calibrator's vapor outlet port. Effects due to backpressure were measured by recording the elemental mercury vapor concentration changes, if any, produced by the calibrators with output flow restrictions. The Thermo 80i atomic fluorescence spectrometer was used. The three calibrators evaluated for this study include the Thermo 81i, Mercury Instruments MC-3000, and Nippon MGS-1. Each calibrator was powered up at least overnight before operation to achieve thermal stability of the equilibrium chamber, and air and/or nitrogen flow was initiated at least one hour before experimental data were gathered.

The design of the calibrator plays an important role in how it responds to flow restrictions. The Mercury Instruments unit employs a vent mechanism to bleed excess pressure. The Nippon unit employs a booster pump as well as a vent. Extreme constrictions in the line or backpressures in excess of recommended operating conditions in these units can ultimately force all of the mercury vapor calibration flow to be vented, resulting in a mercury concentration decrease to zero at the analyzer. For the Thermo unit, backpressure results in a change of dilution air flow through the dilution mass flow controller output to maintain constant concentration.

A range of flow restrictions and resulting backpressures were applied to the outlet ports of the calibrators/generators. The effects were measured at nominal mercury concentration settings of 5 and 30 $\mu\text{g}/\text{m}^3$. These two concentrations were used because the 5 $\mu\text{g}/\text{m}^3$ setting employs a high MFC dilution flow, while the 30 $\mu\text{g}/\text{m}^3$ setting uses a lower flow. The custom jar-style gas sampling manifold was used to provide an introduction device for the analyzer in which vapor temperature and pressure can be measured.

A custom backpressure and measurement apparatus was assembled for this study. Flow restriction and backpressure was applied to the mercury vapor outlet port of the calibrators using a needle valve constructed of PFA (Swagelok P/N PFA-4RPS4). The pressure was measured using a digital pressure indicator (Omega DPI 705) mounted to a Tee situated between the valve and the calibrator's outlet port. A photograph of the device is provided in Figure 8.

Figure 8. Back Pressure Application and Measurement Device

The back of a calibrator is shown on the left, and the needle valve is shown on the right. The valve is designed so that three counterclockwise rotations (1080°) is wide-open, and 45° is almost closed. The valve orientation (position in degrees) was recorded for each experiment.

Mercury Instruments MC-3000 (Mercury Instruments 02) The data obtained for the Mercury Instruments 02 unit at the 5 $\mu\text{g}/\text{m}^3$ nominal setting are presented in Table 7. The pressure ratio values listed at the far right of the table are the outlet pressure divided by the manifold pressure.

Table 7. Mercury Instruments MC-3000 Back Pressure Data at 5 $\mu\text{g}/\text{m}^3$ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp (°F)	80i 5 min ($\mu\text{g}/\text{m}^3$)	Pressure Ratio
1080°	0.7854	0.7793	69.2	7.67880	1.008
720°	0.7855	0.7791	69.8	7.47037	1.008
360°	0.7855	0.7789	70.2	7.63416	1.008
180°	0.7863	0.7787	70.4	7.44981	1.010
90°	0.7886	0.7786	70.8	7.37009	1.012
60°	0.7899	0.7786	71.5	7.42311	1.015
45°	0.7903	0.7786	71.8	6.33105	1.015

The Mercury Instruments MC-3000 employs a vent configuration which releases backpressure. Note that the outlet and manifold pressures change very little as the valve is moved from the open to closed positions. However, when the valve is almost closed at the 45° position, there is a noticeable decrease in the mercury concentration (Figure 9). This is likely due to a condition in which almost all of the output flow has been vented, and little flow is being delivered to the

analyzer. The Thermo 80i atomic fluorescence analyzer is a continuous flow instrument that requires a minimum flow of ~0.3 L/min. Thus, a flow delivered to the analyzer that is <0.3 L/min would result in dilution from outside air at the manifold and a subsequent decrease in measured elemental mercury concentration.

Figure 9. Mercury Instruments MC-3000 Pressure Ratio vs. Concentration at 5 µg/m³ Nominal Setting

An effect on concentration at the lowest three pressure ratios is evident in Figure 9. This could be possibly due to insufficient equilibration time at the low flow condition, or mass flow controller variability. The exact cause of this effect is not known.

The data obtained for the Mercury Instruments MC-3000 calibrator at the 30 µg/m³ nominal setting are presented in Table 8. At this setting, the calibrator is only delivering ~ 1.0 L/min mercury vapor flow with the valve fully open (1080°). At valve positions < 90°, there is a marked decrease in the mercury concentration, presumably due to insufficient flow to the analyzer. Note how the very low flow rate used for this setting produces pressure ratios of that are even lower than those noted in Table 7.

Table 8. Mercury Instruments MC-3000 Back Pressure Data at 30 µg/m³ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp (°F)	80i 5 min (µg/m3)	Pressure Ratio
1080°	0.7816	0.7783	72.3	44.0653	1.004
720°	0.7816	0.7783	72.3	44.2267	1.004
360°	0.7818	0.7783	72.3	44.2090	1.004
180°	0.7822	0.7783	72.4	43.9039	1.005
90°	0.7828	0.7782	72.6	43.6056	1.006
45°	0.7832	0.7780	72.8	33.0921	1.007
30°	0.7833	0.7780	73.2	11.5568	1.007

Figure 10 depicts the pressure ratio vs. mercury concentration conditions for the 30 $\mu\text{g}/\text{m}^3$ nominal setting. Due to the very low flow rate (1.0 L/min) which was delivered to the backpressure device at this setting, it appears likely that an insufficient analyzer flow situation with the valve nearly closed is a likely explanation.

Figure 10. Mercury Instruments MC-3000 Pressure Ratio vs. Concentration at 30 $\mu\text{g}/\text{m}^3$ Nominal Setting

Nippon Instruments Corporation MGS-1 (Nippon 02) The data obtained for the MGS-1 at the 5 $\mu\text{g}/\text{m}^3$ nominal setting are presented in Table 9. The optional booster pump was employed for these studies. The 5 $\mu\text{g}/\text{m}^3$ setting uses a dilution flow of 10 L/min and a booster pump flow rate of 7.0 L/min. Although the booster pump employs a vent mechanism, its purpose is to ensure that a proper flow is delivered through a CEM umbilical to the analyzer (or in this case, the backpressure device).

Table 9. Nippon MGS-1 Back Pressure Data at 5 $\mu\text{g}/\text{m}^3$ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp ($^{\circ}\text{F}$)	80i 5 min ($\mu\text{g}/\text{m}^3$)	Pressure Ratio
1080 $^{\circ}$	0.8324	0.7820	71.7	6.54045	1.064
720 $^{\circ}$	0.8330	0.7820	71.8	6.56802	1.065
360 $^{\circ}$	0.8395	0.7817	72.1	6.59290	1.074
180 $^{\circ}$	0.9574	0.7804	72.5	6.57614	1.227
120 $^{\circ}$	1.360	0.7772	72.8	6.61002	1.750
90 $^{\circ}$	1.573	0.7761	72.9	6.49967	2.027
45 $^{\circ}$	1.678	0.7757	73.0	3.07897	2.163

A plot of the pressure ratio vs. mercury concentration for the 5 $\mu\text{g}/\text{m}^3$ nominal setting is provided in Figure 11. The concentration is consistent up to a pressure ratio of ~ 2.0 . Above a ratio of 2.0, it is not known whether the decrease in elemental mercury concentration is due to

backpressure on the booster pump or whether the decrease in concentration is due to excess venting.

Figure 11. Nippon MGS-1 Pressure Ratio vs. Concentration at 5 µg/m³ Nominal Setting

The data obtained for the MGS-1 at the 30 µg/m³ nominal setting are presented in Table 10. This setting uses a dilution flow rate of 5.0 L/min and a booster pump flow rate of 3.5 L/min. The graph of pressure ratio vs. mercury concentration is provided in Figure 12.

Table 10. Nippon MGS-1 Back Pressure Data at 30 µg/m³ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp (°F)	80i 5 min (µg/m3)	Pressure Ratio
1080°	0.7934	0.7778	68.2	40.1051	1.020
720°	0.7934	0.7776	68.1	40.1218	1.020
360°	0.7943	0.7776	68.3	39.9660	1.021
180°	0.8043	0.7776	68.2	39.9522	1.034
90°	0.8575	0.7776	68.1	39.9146	1.103
75	0.9508	0.7774	67.9	39.7207	1.223
45	1.251	0.7772	67.9	39.7717	1.610
30	1.512	0.7764	68.1	39.3254	1.947

Figure 12. Nippon MGS-1 Pressure Ratio vs. Concentration at 30 µg/m³ Nominal Setting

An effect on concentration at the lowest three pressure ratios is also evident with the MGS-1 at the higher concentration setting.

Thermo 81i (Thermo 03) The data obtained at the 5 µg/m³ nominal setting are presented in Table 11. The 5 µg/m³ setting is a relatively high flow condition, and the effect of closing the valve is observed by an increase in the outlet pressure between the calibrator and the valve. The Thermo 81i is designed to maintain a constant concentration output by adjusting the flow rate of the dilution mass flow controller based on internal pressure transducer measurement of back pressure. As the dilution flow was decreased, there was a slight corresponding drop in the manifold pressure with the ¼-inch vent. Thermo service engineers have indicated that a pressure ratio in excess of 1.6 (9 psi) should not be encountered in the field; however the unit was pushed beyond this limit for the purposes of this experimental study. For the four pressure ratios < 1.6, the mercury concentrations are essentially consistent within ~2 %.

Table 11. Thermo 81i Back Pressure Data at 5 µg/m³ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp (°F)	80i 5 min (µg/m³)	Pressure Ratio
1080°	0.9861	0.7978	77.0	5.73997	1.236
720°	0.9879	0.7976	77.0	5.71883	1.239
360°	0.9983	0.7974	77.0	5.67831	1.252
180°	1.095	0.7949	77.0	5.61216	1.378
90°	1.335	0.7901	77.1	5.49616	1.690
60°	1.888	0.7862	77.1	4.59029	2.401

A duplicate experimental sequence using the 5 µg/m³ setting was performed ~72 hours later. Two additional data sets with the valve in almost-closed configurations were performed for the replicate sequence. The data for the replicate sequence are provided in Table 12. For the four pressure ratios < 1.6, the mercury concentrations are essentially consistent within ~0.5%.

Table 12. Thermo 81i Back Pressure Data at 5 $\mu\text{g}/\text{m}^3$ Nominal Setting (Replicate)

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp ($^{\circ}\text{F}$)	80i 5 min ($\mu\text{g}/\text{m}^3$)	Pressure Ratio
1080 $^{\circ}$	0.9891	0.8011	75.3	5.51000	1.235
720 $^{\circ}$	0.9905	0.8011	75.4	5.50454	1.236
360 $^{\circ}$	1.000	0.8007	75.6	5.50751	1.249
180 $^{\circ}$	1.081	0.7987	75.6	5.47814	1.353
90 $^{\circ}$	1.302	0.7939	75.7	5.41131	1.640
75 $^{\circ}$	1.411	0.7922	75.8	5.36964	1.781
60 $^{\circ}$	1.609	0.7896	75.8	5.31248	2.038
45 $^{\circ}$	1.956	0.7892	75.8	4.39774	2.478

The manually-positioned valve orientation is not a precise setting, so slightly different pressure ratios for nominally identical valve positions are observed. Graphical representations of the pressure ratio vs. mercury concentration for the two 5 $\mu\text{g}/\text{m}^3$ setting experiments are provided in Figures 13 and 14. It should be noted that the initial drop in measured concentration evident in the first experiment is not observed in the replicate experiment. Therefore, it is not a repeatable effect. The results indicate that a better experimental design would be needed to evaluate back pressure effects.

Figure 13. Thermo 81i Pressure Ratio vs. Concentration at 5 $\mu\text{g}/\text{m}^3$ Nominal Setting

Figure 14. Thermo 81i Pressure Ratio vs. Concentration at 5 µg/m³ Nominal Setting (Replicate)

As more extreme backpressure ratios > 1.6 are applied to the calibrator, the effect is a significant decrease in the observed mercury concentration. The absolute concentration differences between the two experiments ~72 hours apart are likely due to the analyzer which was not calibrated during the course of this study.

The data for the 81i at the 30 µg/m³ nominal setting (a lower dilution flow condition) are presented in Table 13, and a graph of the pressure ratio vs. Mercury concentration is provided in Figure 15. The data for the 30 µg/m³ nominal setting were obtained ~48 hours after the Table 11 sequence was performed. For the five pressure ratios < 1.6, the mercury concentration values are consistent within ~4 %.

Table 13. Thermo 81i Back Pressure Data at 30 µg/m³ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp (°F)	80i 5 min (µg/m3)	Pressure Ratio
1080°	0.8871	0.7888	70.3	34.7140	1.125
720°	0.8880	0.7887	70.7	34.0333	1.126
360°	0.8940	0.7887	71.0	33.6722	1.134
180°	0.9483	0.7879	71.4	33.4237	1.204
90°	1.127	0.7855	71.6	33.1924	1.435
75°	1.307	0.7840	72.1	32.9348	1.667
60°	1.462	0.7829	72.3	32.7945	1.867
45°	1.930	0.7817	73.0	27.8581	2.469

Figure 15. Thermo 81i Pressure Ratio vs. Concentration at 30 µg/m³ Nominal Setting

Figure 15 resembles those of the high dilution flow examples provided in Figures 13 and 14. As observed with the Mercury Instruments and Nippon generators, an effect on concentration at the lowest three pressure ratios is evident. This could be possibly due to insufficient equilibration time, or mass flow controller variability, or some other effect. This was observed at least once with all three calibrator units when initial back pressure was applied gradually.

Additional data for the 81i at the 50 µg/m³ nominal setting (the lowest dilution flow condition evaluated) are presented in Table 14. This experiment was conducted ~1 hour after the experimental sequence of Table 11. For this experiment, the sequence was started with the valve in the closed position, and the valve was opened in four steps. For the three pressure ratios < 1.6, the mercury concentrations are essentially consistent within ~3%.

Table 14. Thermo 81i Back Pressure Data at 50 µg/m³ Nominal Setting

Valve	Outlet pressure (atm)	Manifold pressure (atm)	Manifold temp (°F)	80i 5 min (µg/m3)	Pressure Ratio
45°	1.943	0.7780	77.2	51.0583	2.497
90°	1.099	0.7815	77.0	58.2732	1.406
180°	0.9247	0.7835	77.0	56.9588	1.180
360°	0.8842	0.7842	77.2	56.5381	1.128

A corresponding plot of the pressure ratio vs. concentration is provided in Figure 16.

Figure 16. Thermo 81i Pressure Ratio vs. Concentration at 50 $\mu\text{g}/\text{m}^3$ Nominal Setting

As mentioned previously, the design of the Thermo 81i calibrator compensates for back pressure using inlet air at 40 psi and an internal back pressure measurement that feeds back into an adjustment of the dilution mass flow controller to maintain constant concentration. Based on the limited data gathered in this study, the results suggest that at back pressure ratios < 1.6 the 81i calibrator provides relatively consistent concentrations within $\sim 0.2 - 2\%$ at a nominal setting of $5\text{ }\mu\text{g}/\text{m}^3$, within $\sim 4\%$ at a nominal setting of $30\text{ }\mu\text{g}/\text{m}^3$, and within $\sim 3\%$ at a nominal setting of $50\text{ }\mu\text{g}/\text{m}^3$. These variations include the initial drop in concentration observed in the experiments. However, after the initial drop in concentration for the first gradual increase in back pressure at a particular concentration, the phenomenon does not repeat. If this phenomenon did not occur, the observed variability of output concentration due to back pressure could possibly be 1% or less. To explore this further, additional experiments were recommended by Bill Dorko (NIST, Gaithersburg, MD). These additional experiments were conducted as described below toward the goal of defining a more realistic and appropriate procedure for conducting qualification back pressure tests.

Additional Back Pressure Experiments

Follow-up experiments were conducted at WRI by Bill Dorko and Joe Rovani to further evaluate the initial drop in concentration when a set of back pressure studies is begun. Instead of applying a very gradual initial increase in back pressure, Bill Dorko suggested applying step changes rather than gradual changes. By doing this, the initial downward drift was virtually eliminated in the limited number of tests performed. The initial concentration drop with back pressure increase is not observed when the back pressure is cycled between no back pressure applied and back pressure applied at a ratio of 1.8. An example of cycling between no back pressure and high back pressure is provided at the bottom portion (81i $10\text{ }\mu\text{g}/\text{m}^3$ Nominal Setting) of Table 15. By performing the experiment in this manner, the maximum difference in concentration output was only $\sim 2\%$ relative. It is possible that the three generators all work well

within expected umbilical line back pressures (9 psi or less), however, the manner in which the test is conducted may affect the results.

Table 15. Additional 81i Experiments with Back Pressure Valve Cycling.

Backpressure Data (Dorko, Rovani) performed at WRI on Wednesday September 5, 2007: Reference WRI Notebook 1190 Pages 72-74.							
81i 3 ug/m3 Nominal							
Time	Valve	P outlet, mmHg	P manifold, mmHg	P ratio	MFC1, mL/min	MFC2, L/min	80i display, ug/m3
	No valve	790.6	611.8	1.292	7.178	15.810	3.38
8:40	1080°	799.0	611.5	1.307	7.178	15.723	3.33
8:48	720°	802.4	611.4	1.312	7.178	15.674	3.31
8:56	360°	867.3	609.6	1.423	7.178	15.036	3.30
9:04	270°	941.3	607.7	1.549	7.178	14.361	3.28
9:12	180°	1497.0	602.0	2.487	7.178	12.070	2.59
9:36	1080°	799.6	611.6	1.307	7.178	15.706	3.30
9:42	1080°	799.7	611.6	1.308	7.178	15.706	3.28
1. Confirmed previous data that concentration initially drops about 1-2% when operating within acceptable backpressure ranges. 2. Note that MFC2 flow decreases to compensate for increased backpressure, and thus, maintain consistent concentration output.							
81i 50 ug/m3 Nominal							
Time	Valve	P outlet, mmHg	P manifold, mmHg	P ratio	MFC1, mL/min	MFC2, L/min	80i display, ug/m3
10:42	1080°	663.5	594.6	1.116	49.619	8.470	58.0
10:52	720°	664.2	593.9	1.118	49.619	8.459	57.4
11:01	360°	686.1	593.6	1.156	49.619	8.279	57.1
11:10	270°	715.3	594.0	1.204	49.619	8.016	56.8
11:18	180°	952.5	590.7	1.612	49.619	6.340	56.6
11:27	120°	1425.4	589.7	2.417	49.619	4.943	49.4
11:36	1080°	663.8	594.7	1.116	49.619	8.470	56.0
11:46	180°	952.5	591.4	1.611	49.619	6.351	56.0
11:57	1080°	663.7	594.7	1.116	49.619	8.476	55.7
12:07	180°	952.2	591.4	1.610	49.619	6.345	55.8
12:16	1080°	663.8	594.6	1.116	49.619	8.476	55.6
1. Note initial concentration drop as valve is gradually closed; however, when valve is switched back and forth from full open to closed, the concentration appears to equilibrate. 2. MFC2 flow decreases to compensate for increased backpressure; MFC1 flow does not change.							
81i 10 ug/m3 Nominal							
Time	Valve	P outlet, mmHg	P manifold, mmHg	P ratio	MFC1, mL/min	MFC2, L/min	80i display, ug/m3
13:16	1080°	700.8	598.6	1.171	13.602	10.670	11.02
13:30	180°	1080.5	593.0	1.822	13.602	7.704	10.82
13:40	1080°	700.5	598.6	1.170	13.602	10.659	11.00
13:48	180°	1072.7	593.0	1.809	13.602	7.758	10.85
1. At high dilution flows at extreme pressure ratios (1.8 is higher than normally expected), the backpressure effect remains at < 2% relative.							

Based on these results, it appears that for the purposes of the qualification criteria, three back pressure settings will suffice to characterize the ability of each generator to operate in expected umbilical conditions. The backpressure changes should be stepwise between three settings: (1) no back pressure added, (2) 1.3 differential back pressure applied (5 psi) and (3) 1.6 differential back pressure (9 psi). The back pressure, or an equivalent flow restriction corresponding to back pressure for units with pressure vents, can be applied either with sufficient lengths of tubing, or with a PFA (inert) restrictor valve.

The experience gained in these preliminary back pressure experiments led to the successful experimental design used in the Qualification Experiments section of this report. The back pressure tests in the Qualifications Experiments section involve intra-unit nesting between toggled back pressure values in a sequence such as: none, 5 psi, none, 9 psi, none 5 psi, etc. in a short amount of time, so that any relative changes in generator response are immediately evident. These nesting experiments were performed at three concentrations (5, 15, and 30 $\mu\text{g}/\text{m}^3$). The analyzer did not need to be calibrated for these experiments.

Although all of the calibrators evaluated exhibit relatively constant outputs within flow restriction and backpressure ranges which are ranges typically encountered in CEM umbilical lines, in situations where backpressures or flow restrictions are likely to be encountered, it seems prudent that backpressure or volumetric flow should be monitored. All of the calibrators evaluated show mercury concentration decreases due to severe flow restrictions. It would be helpful to the operator of the instrument to know if the calibrator is operating beyond its specifications.

Field Verification of Generator Output

The possibility of using a portable analyzer as a tool to detect generator failures at a power plant site was explored. Experiments were conducted with an Arizona Instruments Model J405 portable mercury vapor monitor. This unit uses thin film gold resistance sensor technology. The sensor circuit board also contains a reference gold element on the opposite side of the analytical sensor, coated with molybdenum, which does not interact with the elemental mercury. These sensors act as two resistors in a Wheatstone bridge. The other two resistors in the bridge are high precision components. Air is drawn through the sensor using a diaphragm pump operating at a nominal flow of 0.75 L/min. This analyzer therefore determines actual $\mu\text{g}/\text{m}^3$ mercury at atmospheric conditions in the fixed volume of air being sampled. There is a carbon filter between the sensor and the diaphragm pump. The gold film sensor element amalgamates with mercury and its resistance changes relative to the reference gold film sensor. The sensor can be periodically regenerated using a 45-minute heating routine. The heating element is external to the sensor. The sensor can only be fully regenerated about 100 times before the mechanical stress of expansion/contraction causes physical damage. Between readings, the sensor is usually not regenerated. Mercury gradually builds up in the gold sensor, and the unit is electronically re-zeroed between readings. The software has a routine that re-sets the zero electronically to read zero before each 30-second sampling/reading cycle. The manufacturer, Arizona Instruments, calibrates the sensor at the factory using VICI elemental mercury permeation tube devices.

For the initial exploratory work with the Jerome J405, a 19-step procedure was devised to incorporate the steps necessary to address the three experiments. When started, the J405 pumps air from the manifold into the unit at a flow rate of 0.75 L/min for 12 seconds (150 mL volume).

The J405 displays the elemental mercury concentration in $\mu\text{g}/\text{m}^3$. Ambient pressure and temperature measurements inside the jar-style manifold were recorded at the start of the experimental sequence. These were taken with no operating flows in or out of the manifold. The ambient pressure is the barometric pressure in Laramie, WY at an altitude of ~7200 feet above sea level. Air flow was initiated by the Thermo 81i calibrator, and the 80i analyzer was zeroed using the zero output from the 81i calibrator. After zeroing the 80i analyzer, zero values were recorded. Data through the manifold were obtained at generator settings of 0, 3, 5, 10, 15, 20, 30, 40, and 50 $\mu\text{g}/\text{m}^3$ to measure the broadest possible range of pressures resulting from the 81i mass flow controller dilution flows. For reference purposes, values were recorded for the 80i mercury concentration ($\mu\text{g}/\text{m}^3$), the Jerome J405 Mercury concentration ($\mu\text{g}/\text{m}^3$), manifold pressure, and manifold temperature through the $\frac{1}{4}$ -inch vent

The initial exploratory investigations indicated that, as for previous work, 8 minutes timeframe per 80i measurement appeared sufficient, with a 5-minute average calculation employed after 3 minutes equilibration time. The manifold did not appear to significantly affect the equilibration time needed between readings. This is plausible considering that for a total mercury vapor source flow as low as 1.0 L/min, a 250 mL jar would be swept four times in the first minute after flow was connected. At lower concentration nominal settings, flows as high as 50 L/min can be expected to sweep the jar 200 times in the first minute. The pressure in the manifold was always slightly above the ambient atmospheric pressure, indicating a positive flow of calibration gas through the manifold.

At the conclusion of the sequence, the zero air flow values were rechecked. Flow was then removed from the manifold and ambient pressure and temperature were rechecked for comparison to the original values. The 19-step sequence and results are provided in Table 16.

Table 16. Nineteen-Step Sequence and Results

Experimental Sequence	Using	80i 5-min avg, $\mu\text{g}/\text{m}^3$	J405, $\mu\text{g}/\text{m}^3$	P, atm	T, °F
1. Record ambient values	Manifold	—	0.00	0.7776	71.8
2. Recalibrate 80i zero using 81i zero air	Manifold	—	—	—	—
3. Record values using 81i zero air	Manifold	0.001638	0.59	0.7928	71.9
4. Record values using 81i zero air	Tee	-0.027450	—	—	—
5. Record values using 81i set to 3 $\mu\text{g}/\text{m}^3$	Manifold	3.57549	2.33	0.8111	72.5
6. Record values using 81i set to 5 $\mu\text{g}/\text{m}^3$	Manifold	5.92448	3.35	0.8013	72.9
7. Record values using 81i set to 5 $\mu\text{g}/\text{m}^3$	Tee	5.98860	—	—	—
8. Record values using 81i set to 10 $\mu\text{g}/\text{m}^3$	Manifold	11.7943	5.75	0.7939	73.3
9. Record values using 81i set to 15 $\mu\text{g}/\text{m}^3$	Manifold	17.6851	8.50	0.7914	73.5
10. Record values using 81i set to 15 $\mu\text{g}/\text{m}^3$	Tee	17.9182	—	—	—
11. Record values using 81i set to 20 $\mu\text{g}/\text{m}^3$	Manifold	23.6116	11.34	0.7904	73.7
12. Record values using 81i set to 30 $\mu\text{g}/\text{m}^3$	Manifold	35.4277	18.31	0.7889	74.0
13. Record values using 81i set to 30 $\mu\text{g}/\text{m}^3$	Tee	35.8401	—	—	—
14. Record values using 81i set to 40 $\mu\text{g}/\text{m}^3$	Manifold	47.2897	25.50	0.7884	74.2
15. Record values using 81i set to 50 $\mu\text{g}/\text{m}^3$	Manifold	59.2391	31.95	0.7882	74.6
16. Record values using 81i set to 50 $\mu\text{g}/\text{m}^3$	Tee	59.7482	—	—	—
17. Record values using 81i zero air	Tee	0.003741	—	—	—
18. Record values using 81i zero air	Manifold	-0.013158	0.57	0.7928	74.8
19. Record ambient values	Manifold	—	0.00	0.7776	75.0

The outputs of the Thermo 80i continuous atomic fluorescence analyzer and Jerome J405 $\mu\text{g}/\text{m}^3$ results are compared (in blue) in Figure 17. The black trend line shows a linear correlation between the two analyzers. The Thermo 80i measures actual vppb and converts this to $\mu\text{g}/\text{m}^3$ corresponding to standard conditions, while the Jerome J405 measures actual $\mu\text{g}/\text{m}^3$.

Figure 17. Thermo 80i vs. Jerome J405 Concentration Results

The short and long term stability and variability of the J405 portable analyzer was investigated in experiments with the MC-3000 and 80i generators. The experiments were designed to investigate the potential use of the J405 as a portable device to rapidly check for proper performance of a generator unit in the field. These studies also yielded quantitative information as to the intra-day stability of the Thermo 80i spectrometer output, and the intra-day stability of generator concentration output. For these studies, the generators were powered at least overnight to maintain temperatures in the equilibrium chambers. Air flow to the generator was initiated in the morning at least one hour before measurements were begun.

An initial set of measurements was made to compare the output from the Jerome J405 analyzer with the Thermo 80i spectrometer using the glass jar manifold and a Mercury Instruments MC-3000 elemental mercury generator set at three different concentrations: 5, 15, and 30 $\mu\text{g}/\text{m}^3$. Data were collected over a 9-day timeframe using 20 repetitive measurements at a single concentration during a three-hour period. Each concentration was analyzed in triplicate. Plots of the results at the three concentrations are provided in Figures 18-20. The data show the variability of each analyzer relative to the set point of the generator. The output of the Jerome J405 unit slowly increases relative to the output of the Thermo 80i spectrometer over the 3-hour period. This occurred at all three concentrations for every day in which the study was performed. This is probably a function of the short cycle gold amalgam regeneration. Because of the results, it is uncertain how each unit contributed individually to the observed changes. However, it seems that within some undefined uncertainty, the analyzers can change within some variability (to be defined) during the course of repeated measurements.

Figure 18. Mercury Instruments MC-3000 at 5 $\mu\text{g}/\text{m}^3$ Monitored with Jerome J405 and Thermo 80i Analyzers

Figure 19. Mercury Instruments MC-3000 at 15 $\mu\text{g}/\text{m}^3$ Monitored with Jerome J405 and Thermo 80i Analyzers

Figure 20. Mercury Instruments MC-3000 at 30 $\mu\text{g}/\text{m}^3$ Monitored with Jerome J405 and Thermo 80i Analyzers

Experiments were repeated using the MC-3000 after it had been running with air flow all night. The results also showed evidence of drift of the Jerome unit relative to the Thermo 80i unit (Figure 21). There was significant scatter over several percent in the data for both analyzers during the course of the study. This could be attributed to generator variability, analyzer variability, or both. The results show essentially no difference in results if the generator air was on all night or only for one hour before readings were taken.

Figure 21. Mercury Instruments MC-3000 With Overnight Air Flow Equilibration at 5 $\mu\text{g}/\text{m}^3$ Monitored with Jerome J405 and Thermo 80i Analyzers

The Jerome J405 gold amalgam film analyzer was typically conditioned with a 45-minute thermal sensor regeneration procedure at the beginning of each day, and measurements of concentrations of generator output were repeatedly taken during each day at 8-minute intervals without sensor regeneration. To explore the effect of the gradual buildup of mercury in the gold film, a series of measurements at 30-second intervals was obtained from a flow stream set at 5 $\mu\text{g}/\text{m}^3$ from the MC-3000 generator. The results showed a rapid climb in reading values over the 8 minute period in which repeated 30-second readings were taken. When the reading interval was increased again to 8 minutes, a drop in the values was noted (Figure 22).

Similar experiments were repeated with a Thermo 81i generator. In one set of experiments, the generator was powered continuously to maintain operating temperature of the equilibrium chamber, and the air flow was initiated twenty-five hours before data collection began. In the second set of experiments, the generator was powered overnight and the air flow was initiated one hour before data collection began. Data collection was performed over a three-hour period for each set of runs. The results show no significant difference due to duration of air flow (Figure 23).

Figure 22. Jerome J405 Readout Values at 30 Second Intervals for an 8-Minute Period

Figure 23. Thermo 81i With 25-Hour, and One-Hour Air Flow Times at 5 $\mu\text{g}/\text{m}^3$ Monitored with Jerome J405 and Thermo 80i Analyzers

Experiments with the Thermo 81i generator at a $30 \mu\text{g}/\text{m}^3$ nominal set point were conducted also. Power was left on continually to maintain temperature in the equilibrium chamber. The air flow in one experiment was initiated 49 hours before the sequence was begun, and in the other experiment, the air flow was initiated only 1 hour before measurements began. As before, the duration of air flow did not result in any significant difference in results (Figure 24). During the 49-hour experiment, the 8-minute measurement sequence was interrupted, and the Jerome J405 sensor was conditioned using a 45-minute manufacturer's procedure to thermally remove mercury from the sensor. Jerome J405 data point 11 was taken immediately after sensor conditioning (Figure 24, top). The output of the portable analyzer dropped significantly due to the conditioning. During the sequence with the one-hour air flow at $30 \mu\text{g}/\text{m}^3$, the Jerome J405 thermal sensor regeneration sequence was performed twice (Figure 24 bottom, data points 11 and 15), with the same general result. Variability in the Jerome J405 output is apparently due to accumulation of mercury in the gold sensor element. Variability in the J405 can also be partially due to variations in the $0.75 \text{ L}/\text{min}$ diaphragm pump flow rate.

Figure 24. Thermo 81i With 49-Hour, and One-Hour Air Flow Times at $5 \mu\text{g}/\text{m}^3$ Monitored with Jerome J405 and Thermo 80i Analyzer

Assuming that the Thermo 80i spectrometer is stable for each 3-hour measurement period within the days of the comparison study, the observed variability can be assumed to be attributed to the generators alone. For the entire study, the Thermo 81i generator inter-day drift ranged from 1.1-1.9% relative (Figures 23-24). The MC-3000 generator inter-day drift ranged from 1.2-16.1% relative (Figures 18-21).

Table 17. Summary of Variability Results for Mercury Instruments MC-3000 and Thermo 81i Generators Evaluated with Jerome J405 and Thermo 80i Analyzers

Day to Day Variability - Initial Reading for Day, $\mu\text{g}/\text{m}^3$				
$\mu\text{g}/\text{m}^3$	Date	Jerome J405	Thermo 80i	J405/80i Ratio
MC 3000				
5	8/13/07	6.53	12.7	0.513
5	8/15/07	6.04	11.6	0.522
5	8/20/07	6.04	11.5	0.527
5	10/5/07	6.77	11.1	0.610
Max % Difference		12.1	14.7	18.9
15	8/14/07	15.98	26.7	0.599
15	8/17/07	16.10	27.0	0.597
15	8/22/07	16.97	26.5	0.640
Max % Difference		6.20	1.78	9.10
30	8/16/07	36.2	52.1	0.695
30	8/21/07	36.4	52.5	0.694
30	8/23/07	34.2	46.6	0.734
Max % Difference		6.43	12.70	5.76
Thermo 81i				
5	6/19/07	3.35	5.92	0.565
5	10/8/07	4.08	5.48	0.745
5	10/9/07	4.02	5.47	0.735
Max % Difference		21.8	8.22	31.80
30	6/19/07	18.3	35.4	0.517
30	10/10/07	24.7	32.8	0.753
30	10/11/07	25.1	32.8	0.765
Max % Difference		37.20	7.93	48.00

The results from the study with the MC-3000 and 81i generators and the J405 and 80i analyzers show that both analyzers exhibit some drift over several days elapsed time, assuming repeatable generator output, as shown in Table 17. The Thermo 80i can be calibrated by the user, so this is not a problem. However, the Jerome J405 can not be calibrated by the user. Its original intended use is as an industrial hygiene monitor and it can only be calibrated by the manufacturer in the factory in Tempe, AZ. The response of the J405 analyzer sensor relative to the response of the uncalibrated 80i spectrometer changes with time. A plot of the initial reading of each day for both analyzers in chronological order spanning experiments conducted from June

19 to October 10, 2007 shows that the response ratio increases significantly over time (Figure 25). This relative variability can not be attributed to output variability or drift. An examination of the source data in Table 7 suggests that the day to day variation and drift of the J405 is greater than the day to day variation and drift of the 80i.

Figure 25. Variation and Drift of Jerome J405 Response to Thermo 80i Response Over Four Months

For the Jerome J405 analyzer to be considered as a possible elemental mercury generator output verification device, the variability, both day to day and inter day will need to be decreased significantly. The sampling pump could be replaced with a mass flow controller system. The calibration of the gold film sensor could be improved as a function of the gold loading in the film. The analyzer then would become a vppb analyzer with very accurate molar air flow across the sensor instead of a $\mu\text{g}/\text{m}^3$ analyzer. The remaining issue would be the stability and repeatability of the sensor itself for repeated measurements. Since the sensor can only be thermally regenerated about 100 times before the sensor element is damaged mechanically due to repeated thermal expansion and contraction, calibration of the sensor must accurately accommodate the gradual buildup of mercury in the sensor element before, after, and between thermal regeneration cycles.

Other rapid and cost effective approaches of verifying generator output in the field need to be explored also. These include sorbent trap testing (30B Method 2-section carbon traps), and nesting analysis against standard gas cylinders or reference generators. We do not know the

inherent variability or uncertainty associated with these approaches, so it is too early to recommend a preferred procedure. The relative merits and drawbacks of each approach need to be evaluated carefully.

QUALIFICATION EXPERIMENTS

According to the August 2007 Interim Traceability Protocol, the elemental mercury generator qualification experiments that must be performed by the vendors include evaluation of the effects of several variables on generator concentration output (EPA 2007). These include back pressure, ambient pressure, temperature, and line voltage. The qualification test criteria should be written to be very specific in what is needed, yet relatively simple to perform. It will be important to define exactly what data need to be obtained with each experiment, with some guidance as to how the tests should be conducted. This will eliminate confusion amongst the vendors, who would prefer not to generate data only to find later that it is not sufficient. The vendors are seeking a protocol that spells out exactly what they need to do. The protocol also should provide equations to calculate the percent variability values. Once data are generated, values that are reasonable and achievable should be used as acceptance criteria in a revised protocol. The purpose of the qualification tests is to rapidly evaluate and document that a vendor design performs as required. Qualification tests will eliminate models of units where the design is not adequate for mercury cap and trade CEM analyzer calibration.

Experimental schemes using a simple series of 3 x 3 matrices (3 concentrations, 3 variable conditions) for each variable were evaluated. Generator output was evaluated using three nominal concentration settings of 5, 15, and 30 $\mu\text{g}/\text{m}^3$. The variables included back pressure, ambient external operating pressure, ambient external operating temperature, and line voltage. For back pressure, the conditions were no pressure applied, 5 psi, and 9 psi applied. CEM umbilicals are not expected to cause greater than 9 psi back pressure. For generators that vent excess pressure, equivalent flow restrictions were used. Back pressure experiments did not require nesting of two separate generators. Nesting was achieved by toggling the back pressure between the three values for a particular generator and recording the output with a spectrometer. For external pressure evaluation, the generator being evaluated was placed in a pressure-controlled chamber, and a nesting analysis was performed against another generator outside the chamber. Pressures evaluated were 0.78, 0.95, and 1.1 atm. For ambient external operating temperature evaluation, the generator being evaluated was placed in a temperature-controlled chamber, and a nesting analysis was performed against another generator outside the chamber. Three temperatures were studied: 10, 20, and 30 °C. Line voltage effects were studied using a Variac unit. Experiments were conducted at three line voltage settings: 105, 115, and 125 Volts. Line voltage testing was initially performed using an intra-unit nesting sequence by toggling an individual generator between the three line voltages. Subsequent line voltage testing was also performed using inter-unit nesting sequences where the tested generator was evaluated side by side with a control generator.

3/8-inch Atmospheric Dump Vent

The atmospheric dump utilized in initial exploratory studies was a three-way PFA Tee with 1/4-inch PFA tubing used for all three arms of the tee. To relieve any backpressure effects to the Thermo 80i analyzer which may have been caused by this setup, the vent arm was drilled to accommodate a larger diameter 3/8-inch vent. A 6-inch length of Tygon was used for the vent arm, which was held in place with a clamp that held the tubing without pinching it or causing any other restriction. The Tygon tubing was placed just below the inlet of a 3-inch diameter aluminum duct with a blower to exhaust vented vapor. A photo of the 3/8-inch vent setup located at the rear of the Thermo 80i analyzer is shown in Figure 26.

Figure 26. 3/8-Inch Atmospheric Dump Configuration

To investigate if the 3/8 inch vent setup was providing a true atmospheric dump, a Thermo 81i calibrator was installed as the Hg vapor source. The Hg output tubing from the 81i is visible in the lower right of the photo. The analyzer chamber pressures were noted for a variety of calibrator flow rates and concentrations. For each calibrator setting, the 80i optical chamber pressure (~24 mm Hg) and chamber flow were consistent. After these changes were made to the atmospheric vent, the response profiles (linearity) for each calibrator were re-established.

Generator/Calibrator Output Profiles Using The 3/8-Inch Vent

The Hg response profiles for the calibrators were determined for nine nominal concentration settings ranging from 3 to 30 $\mu\text{g}/\text{m}^3$. The data for the Mercury Instruments MC-3000 unit are presented in Table 18 and plotted in Figure 27.

Table 18. Mercury Instruments MC-3000 Linearity Data Using 3/8" Vent

MC-3000	Setpoint, $\mu\text{g}/\text{m}^3$ Nominal	80i $\mu\text{g}/\text{m}^3$, 5-min avg	80i chamber, mm Hg	~Flow Rate To 3/8" Atmospheric Dump
1	3.00	5.10	24.24	2 L/min
2	4.00	5.98	24.24	2 L/min
3	5.00	7.07	23.94	2 L/min
4	7.50	10.85	23.94	2 L/min
5	10.00	14.32	23.94	2 L/min
6	12.50	18.01	23.94	2 L/min
7	15.00	21.51	23.94	2 L/min
8	20.00	28.47	23.94	2 L/min
9	30.00	43.13	23.94	1 L/min

Figure 27. Linear Response Profile for Mercury Instruments MC-3000 Using 3/8" Vent

The MC-3000 employs an internal vent setup that diverts a portion of the total flow rate to a charcoal scrubber vent, and the flow rates indicated in the table are $\sim 40\%$ of the total flow.

Linearity results for the Thermo 02 81i generator are presented in Table 19 and plotted in Figure 28.

Table 19. Thermo 81i - 02 Linearity Data Using 3/8" Vent

Thermo02 81i	Setpoint, µg/m3 Nominal	80i µg/m3, 5-min avg	80i chamber, mm Hg	~Flow Rate To 3/8" Atmospheric Dump
1	3.00	3.16	23.94	16.1 L/min
2	4.00	4.20	24.24	14.5 L/min
3	5.00	5.24	23.94	13.4 L/min
4	7.50	7.88	23.94	11.8 L/min
5	10.00	10.50	23.94	11.0 L/min
6	12.50	13.11	23.94	10.4 L/min
7	15.00	15.67	23.94	10.1 L/min
8	20.00	20.70	23.94	9.6 L/min
9	30.00	30.05	23.94	9.1 L/min

Figure 28. Linear Response Profile for Thermo 81i - 02 Using 3/8" Vent

The flow rates delivered by the 81i depend on the length of ¼-inch tubing used to deliver the Hg vapor to the analyzer. The length of tubing provides a restriction to flow, which is investigated and described in the Back Pressure sections of this report. The length of tubing used for every calibrator was kept as a constant, and was 7 feet for these studies.

Linearity results for the Thermo 03 81i generator are presented in Table 20 and plotted in Figure 29. Since the volumetric flow rates were already determined for this calibrator model (Table 19) they were not included in this data set.

Table 20. Thermo 81i - 03 Linearity Data Using 3/8" Ven

Thermo03 81i	Setpoint, µg/m3 Nominal	80i µg/m3, 5-min avg	80i chamber, mm Hg
1	3.00	3.12	23.94
2	4.00	4.22	23.94
3	5.00	5.30	23.94
4	7.50	8.01	23.94
5	10.00	10.73	23.94
6	12.50	13.44	23.65
7	15.00	16.14	23.94
8	20.00	21.63	23.94
9	30.00	32.56	23.94

Figure 29. Linear Response Profile for Thermo 81i - 03 Using 3/8" Vent

For the Nippon MGS-1, a fresh droplet of Hg had to be added to the Hg source so that it would be operational. The calibrator was utilized in configuration with its booster pump. Linearity results for the Nippon MGS-1 generator are presented in Table 62.21 and plotted in Figure 62.30. The flow rates listed in the data below are those delivered by the booster pump setting.

Table 21. Nippon MGS-1 Linearity Data Using 3/8" Vent

Nippon MGS-1	Setpoint, µg/m3 Nominal	80i µg/m3, 5-min avg	80i chamber, mm Hg	~Flow Rate To 3/8" Atmospheric Dump
1	2.98	4.29	23.94	7 L/min
2	4.66	6.71	23.94	5 L/min
3	5.33	7.69	23.65	5 L/min
4	7.46	10.78	23.94	3 L/min
5	9.33	13.26	23.94	3 L/min
6	11.19	14.83	23.94	7 L/min
7	15.99	21.53	23.94	5 L/min
8	22.38	30.29	23.94	3 L/min
9	29.84	39.28	23.65	3 L/min

Figure 30. Linear Response Profile for Nippon MGS-1 Using 3/8" Vent

The following conclusions can be made from the response profiles (linearity) using the 3/8-inch vent setup:

1. The generators/calibrators all produce highly linear outputs.
2. The slopes of the responses are different (from 1.0 to 1.4) for each calibrator. This is likely due to the two different platforms (constant vppb, constant $\mu\text{g}/\text{m}^3$) of the units operating at 7,200 feet (0.78 atm.), and different vapor pressure equations utilized by the different vendor units.
3. The ranges of flow rates from 1 L/min to 16 L/min showed virtually no effect on the 80i analyzer optical chamber pressure, which confirm the efficiency of the 3/8-inch vent.

Effect of Back Pressure on Generator/Calibrator Output

The back pressures applied to the calibrators/generators were intended to simulate field conditions where long lengths of tubing, such as those used for umbilical lines for CEM probes, may apply a backpressure as high as 0.6 atm (9 psi) to a calibrator's vapor outlet port. Effects due to backpressure were measured by recording the Hg vapor concentration changes, if any, produced by the calibrators with output flow restrictions. The backpressure and measurement device evaluated and described previously in the Output Characteristics section of this report was used for this study. However, it was reconfigured with the 3/8-inch vent. A photo of the back pressure device is provided in Figure 31 in which the 3/8-inch vent is evident in the right side of the photo.

Figure 31. Back Pressure Experiment Readout, Valve, and Vent

In this photo, the calibrator is located to the far left and the analyzer is located to the far right. The valve is designed so that three counter-clockwise rotations of the handle correspond to a wide-open valve. Three backpressure conditions were applied in bracketed sequences of 15-minute intervals for three nominal concentration settings. The bracketed sequence and experimental results for the Thermo02 81i calibrator are presented in Table 22.

The amount of backpressure was read at the digital pressure indicator. The pressure ratios in the table are indicative of the relative amounts of backpressure applied above the ambient backpressure (valve wide open). The nested relative percent difference values are a measure of the backpressure effect on concentration output. The concentration results are in good agreement with the linear response profiles generated earlier in which the slope was determined to be 1.00 (Figure 28). The dilution flow rate listed on the far right of the table shows that the 81i compensates for flow restriction by lowering the dilution flow output. These data were obtained with the backpressure applied to the Cal Gas outlet port of the 81i.

Table 22. Thermo 81i - 02 Cal Gas Outlet Back Pressure Data

Thermo02 81i Cal Gas Port	Valve	Backpressure, mmHg	Pressure Ratio	80i 5-min avg, µg/m3	Nested Rel. % Diff.	81i MFC2 (Dil) Flow
5.00 µg/m3 Nominal	3 rotations open	605.6	1.00	5.16		
	7/8 rotation open	785.5	1.30	5.14	0.1%	
	5/8 rotation open	962.1	1.59	5.12	0.5%	
	3 rotations open	605.7	1.00	5.13		
	7/8 rotation open	783.8	1.29	5.12	0.1%	
	5/8 rotation open	964.0	1.59	5.11	0.3%	
	3 rotations open	605.7	1.00	5.12		14.1 L/min
	7/8 rotation open	783.9	1.29	5.13	0.1%	12.5 L/min
	5/8 rotation open	972.0	1.60	5.10	0.5%	10.9 L/min
	3 rotations open	605.6	1.00	5.13		14.1 L/min
15.00 µg/m3 Nominal	3 rotations open	596.7	1.00	15.27		
	7/8 rotation open	792.7	1.33	15.32	0.4%	
	5/8 rotation open	890.4	1.49	15.35	0.6%	
	3 rotations open	596.5	1.00	15.25		
	7/8 rotation open	785.6	1.32	15.28	0.3%	
	5/8 rotation open	966.8	1.62	15.28	0.3%	
	3 rotations open	596.0	1.00	15.22		10.6 L/min
	7/8 rotation open	776.8	1.30	15.26	0.4%	9.0 L/min
	5/8 rotation open	939.3	1.58	15.32	0.8%	7.8 L/min
	3 rotations open	596.2	1.00	15.19		10.6 L/min
30.00 µg/m3 Nominal	3 rotations open	594.0	1.00	30.12		
	7/8 rotation open	770.9	1.30	30.27	0.7%	
	5/8 rotation open	944.2	1.59	30.32	0.8%	
	3 rotations open	594.2	1.00	30.02		
	7/8 rotation open	768.7	1.29	30.28	1.0%	
	5/8 rotation open	950.7	1.60	30.29	1.0%	
	3 rotations open	594.0	1.00	29.95		9.5 L/min
	7/8 rotation open	774.6	1.30	30.17	0.8%	8.0 L/min
	5/8 rotation open	953.1	1.60	30.23	1.0%	6.8 L/min
	3 rotations open	594.0	1.00	29.91		9.5 L/min

Alternately, the Probe Port outlet was used; these data are presented in Table 23. The cal gas port is connected to an internal 3 psi pressure relief valve and the excess pressure is vented through a carbon sorbent bed. With the Probe Port outlet, the internal check valve with 3 psi crack pressure limits the amount of backpressure that can be applied to the calibrator. Therefore, the backpressure applied at the 5/8 rotation position is actually less than that applied at the 7/8 position. The effect of the internal vent is evident in the flow rate data. The concentration results are also in agreement with the previous response profile data (Figure 28). The nested relative percent differences indicate that the effects of back pressure on concentration were measured at 0.6% or less for the low concentration sequences, and at 1.0% or less for the high concentration sequences.

Table 23. Thermo 81i -02 Probe Port Outlet Back Pressure Data

Thermo02 81i Probe Port	Valve	Backpressure, mmHg	Pressure Ratio	80i 5-min avg, µg/m3	Nested Rel. % Diff.	81i MFC2 (Dil) Flow
5.00 µg/m3 Nominal	3 rotations open	605.2	1.00	5.19		
	7/8 rotation open	781.5	1.29	5.15	0.4%	
	5/8 rotation open*	740.8	1.22	5.14	0.6%	
	3 rotations open	605.6	1.00	5.15		
	7/8 rotation open	793.0	1.31	5.13	0.1%	
	5/8 rotation open*	763.7	1.26	5.11	0.3%	
	3 rotations open	605.9	1.00	5.12		14.5 L/min
	7/8 rotation open	780.6	1.29	5.12	0.1%	12.8 L/min
	5/8 rotation open*	761.8	1.26	5.12	0.1%	13.0 L/min
	3 rotations open	606.1	1.00	5.13		14.5 L/min
15.00 µg/m3 Nominal	3 rotations open	597.9	1.00	15.38		
	7/8 rotation open	772.6	1.29	15.35	0.2%	
	5/8 rotation open*	707.0	1.18	15.32	0.03%	
	3 rotations open	597.7	1.00	15.27		
	7/8 rotation open	781.5	1.31	15.29	0.3%	
	5/8 rotation open*	684.1	1.14	15.25	0.03%	
	3 rotations open	597.3	1.00	15.22		10.8 L/min
	7/8 rotation open	763.4	1.28	15.23	0.2%	9.2 L/min
	5/8 rotation open*	680.9	1.14	15.20	0.0%	10.0 L/min
	3 rotations open	597.2	1.00	15.18		10.8 L/min
30.00 µg/m3 Nominal	3 rotations open	594.9	1.00	30.12		
	7/8 rotation open	768.4	1.29	30.33	1.0%	
	5/8 rotation open*	677.2	1.14	30.16	0.4%	
	3 rotations open	594.9	1.00	29.96		
	7/8 rotation open	766.1	1.29	30.20	1.0%	
	5/8 rotation open*	678.2	1.14	30.02	0.4%	
	3 rotations open	594.9	1.00	29.86		9.7 L/min
	7/8 rotation open	752.3	1.26	30.08	0.9%	8.3 L/min
	5/8 rotation open*	666.1	1.12	29.91	0.3%	9.0 L/min
	3 rotations open	594.7	1.00	29.77		9.7 L/min

The backpressure data for the Mercury Instruments MC-3000 are presented in Table 24. Since this unit uses an internal tee vent which releases backpressure through a carbon sorbent tube, the backpressures change very little as the valve is moved from the open to closed positions. The flow listed at the far left of the table indicates the calibrator set point flow, not the actual flow delivered to the analyzer. If the valve is closed further than $\frac{3}{4}$ rotation, there is a significant decrease in the Hg concentration measured by the analyzer. This is likely due to a condition in which almost all of the output flow has been vented, with little flow delivered to the analyzer. This behavior was observed and described earlier in this report.

Table 24. Mercury Instruments MC-3000 Back Pressure Data

Mercury Instr.02 MC-3000	Valve Position	Backpressure, mmHg	Pressure Ratio	80i 5-min avg, µg/m3	Nested Rel. % Diff.	Flow Setpoint*
5.00 µg/m3 Nominal	3 rotations open	587.3	1.000	6.96		
	1 rotation open	589.3	1.003	7.06	1.4%	
	3/4 rotation open	590.6	1.006	6.99	0.4%	
	3 rotations open	587.3	1.000	6.97		
	1 rotation open	588.6	1.002	7.04	0.4%	
	3/4 rotation open	591.0	1.006	7.11	0.6%	
	3 rotations open	587.3	1.000	7.17		5.0 L/min
	1 rotation open	589.3	1.003	7.13	1.1%	5.0 L/min
	3/4 rotation open	590.6	1.006	6.95	1.5%	5.0 L/min
	3 rotations open	587.3	1.000	6.94		5.0 L/min
15.00 µg/m3 Nominal	3 rotations open	587.3	1.000	20.84		
	1 rotation open	588.5	1.002	20.93	0.1%	
	3/4 rotation open	590.5	1.005	20.83	0.3%	
	3 rotations open	587.0	1.000	20.96		
	1 rotation open	588.8	1.003	20.80	0.8%	
	3/4 rotation open	589.9	1.005	20.99	0.1%	
	3 rotations open	587.0	1.000	20.97		4.0 L/min
	1 rotation open	588.2	1.002	20.98	0.1%	4.0 L/min
	3/4 rotation open	589.7	1.005	20.84	0.6%	4.0 L/min
	3 rotations open	586.0	1.000	20.96		4.0 L/min
30.00 µg/m3 Nominal	3 rotations open	585.3	1.000	42.05		
	1 rotation open	586.3	1.002	42.30	0.4%	
	3/4 rotation open	587.2	1.003	41.86	0.6%	
	3 rotations open	585.5	1.000	42.20		
	1 rotation open	587.0	1.003	42.05	0.3%	
	3/4 rotation open	587.7	1.004	41.60	0.8%	
	3 rotations open	585.8	1.000	41.64		2.5 L/min
	1 rotation open	586.5	1.001	41.71	0.1%	2.5 L/min
	3/4 rotation open	587.8	1.003	41.75	0.2%	2.5 L/min
	3 rotations open	585.8	1.000	41.71		2.5 L/min

The linearity of the concentration data are in agreement with the previous response profile (Figure 27). The effects of the flow restrictions are 1.5% or less at the low concentration condition and 0.8% or less at the high concentration condition.

The data for the Nippon MGS-1 generator are presented in Table 25. For the most part, the backpressures do not significantly affect the precision of the output Hg concentrations. However, there is a serious discrepancy between these results and the previous response profile (Figure 30). This behavior has been noticed with previous usage of the instrument, and is likely due to contamination of the very small surface area liquid mercury droplet in the equilibrium chamber. Removal of the droplet and replacement with new elemental Hg would restore the unit's capability; however, the unit was in operation only 7 days before it showed reduced performance characteristics. During this entire time, the droplet was exposed only to ultra high purity nitrogen as specified by the vendor. For this reason, the Nippon unit was not used in subsequent qualification testing.

Table 25. Nippon MGS-1 Back Pressure Data

Nippon02 MGS-1	Valve Position	Backpressure, mmHg	Pressure Ratio	80i 5-min avg, $\mu\text{g}/\text{m}^3$	Nested Rel. % Diff.	Booster Pump Flow
4.90 $\mu\text{g}/\text{m}^3$ Nominal	3 rotations open	585.0	1.00	6.38		
	7/16 rotation open	760.5	1.30	6.38	0.1%	
	5/16 rotation open	946.0	1.62	6.39	0.1%	
	3 rotations open	585.0	1.00	6.39		
	7/16 rotation open	757.3	1.29	6.35	1.9%	
	5/16 rotation open	931.6	1.59	6.43	0.6%	
	3 rotations open	584.8	1.00	6.55		~5 L/min
	7/16 rotation open	755.5	1.29	6.49	0.1%	~4 L/min
	5/16 rotation open	941.4	1.61	6.44	0.7%	~3 L/min
	3 rotations open	584.6	1.00	6.42		~5 L/min
14.92 $\mu\text{g}/\text{m}^3$ Nominal	3 rotations open	584.6	1.00	15.01		
	7/16 rotation open	757.8	1.30	14.98	0.2%	
	5/16 rotation open	931.9	1.59	15.01	0.4%	
	3 rotations open	584.4	1.00	14.88		
	7/16 rotation open	753.4	1.29	14.86	1.1%	
	5/16 rotation open	937.6	1.60	14.74	0.2%	
	3 rotations open	584.2	1.00	14.53		~5 L/min
	7/16 rotation open	761.5	1.30	14.41	0.04%	~4 L/min
	5/16 rotation open	936.4	1.60	14.38	0.2%	~3 L/min
	3 rotations open	584.0	1.00	14.30		~5 L/min
29.84 $\mu\text{g}/\text{m}^3$ Nominal	3 rotations open	582.0	1.00	25.42		
	7/16 rotation open	764.2	1.31	27.12	3.7%	
	5/16 rotation open	937.8	1.61	28.07	7.4%	
	3 rotations open	581.9	1.00	26.86		
	7/16 rotation open	751.5	1.29	26.38	0.3%	
	5/16 rotation open	933.0	1.60	26.21	0.1%	
	3 rotations open	581.9	1.00	26.08		~3 L/min
	7/16 rotation open	745.6	1.28	26.05	0.8%	~2.5 L/min
	5/16 rotation open	930.9	1.60	25.73	0.4%	~2 L/min
	3 rotations open	581.8	1.00	25.59		~3 L/min

Effect of Line Voltage on Generator/Calibrator Output

A Variac Model TDGC-2KM was used to alter the line voltage for the calibrators. A photo of the Variac with a Thermo 81i calibrator is provided in Figure 32. The probe tips of a Fluke Model 79 multimeter were inserted in the unused outlet of the Variac to measure line voltage. The Variac was dialed to 105.0 ± 0.1 , 115.0 ± 0.1 , and 125.0 ± 0.1 VAC. The experimental sequence used was an intra-unit sequence (testing performed on one unit at a time) similar to that used for back pressure. The concentration results for test conditions of 105 and 125 VAC were nested within brackets of 115 VAC control conditions. The relative percent difference values were calculated. Ten-minute equilibration timeframes were used between readings. The experimental sequence used and the concentration data from the Cal Gas port of the Thermo02 calibrator unit are provided in Table 26.

Figure 32. Variac Unit for Line Voltage Experiments

Table 26. Thermo 81i - 02 Line Voltage Variation Data

Thermo02 81i Cal Gas Port	Line VAC ($\pm 0.1V$)	80i 5-min avg, $\mu g/m^3$	Nested Rel. % Diff.
5.00 $\mu g/m^3$ Nominal	115.0	4.90	
	105.0	4.89	0.2%
	125.0	4.86	0.4%
	115.0	4.86	
	105.0	4.85	0.2%
	125.0	4.85	0.2%
	115.0	4.86	
	105.0	4.84	0.3%
	125.0	4.83	0.3%
	115.0	4.83	
15.00 $\mu g/m^3$ Nominal	115.0	14.68	
	105.0	14.66	0.1%
	125.0	14.64	0.03%
	115.0	14.61	
	105.0	14.60	0.1%
	125.0	14.60	0.1%
	115.0	14.57	
	105.0	14.57	0.1%
	125.0	14.56	0.0%
	115.0	14.55	
30.00 $\mu g/m^3$ Nominal	115.0	28.65	
	105.0	28.61	0.04%
	125.0	28.59	0.04%
	115.0	28.55	
	105.0	28.52	0.02%
	125.0	28.50	0.05%
	115.0	28.48	
	105.0	28.48	0.1%
	125.0	28.46	0.1%
	115.0	28.41	

Although the effect of line voltage as determined by the change in nested relative % difference results is almost negligible, there is a noticeable downward drift in the concentration results. The line voltage test was repeated using an inter-unit sequence (testing performed using one unit as a test case and another unit as a control). The Thermo03 calibrator was used as the control instrument (ambient line voltage) and the Thermo02 unit was used as the test instrument. The results for a nominal concentration setting of 15 $\mu\text{g}/\text{m}^3$ are presented in Table 27.

The downward drift is evident again but it is observed in both calibrators. Nested ratios were calculated for each test condition vs. its bracketed control conditions. The nested ratio stays virtually identical so the drift is identical to both calibrators. This suggests that the analyzer is the likely cause of the apparent drift.

Table 27. Thermo 81i -02 Nested Line Voltage Variation Data

Calibrator	Line VAC ($\pm 0.1\text{V}$)	80i 5-min avg. $\mu\text{g}/\text{m}^3$	<u>Nested Ratio</u>
Thermo03	ambient	15.55	0.957
Thermo02	115.0	14.86	
Thermo03	ambient	15.52	0.956
Thermo02	105.0	14.84	
Thermo03	ambient	15.51	0.957
Thermo02	125.0	14.83	
Thermo03	ambient	15.49	0.956
Thermo02	115.0	14.81	
Thermo03	ambient	15.48	0.957
Thermo02	105.0	14.81	
Thermo03	ambient	15.47	0.957
Thermo02	125.0	14.80	
Thermo03	ambient	15.47	

The line voltage data for the MC-3000 are presented in Table 28. These data were also generated using the intra-unit nesting procedure. The average of the nested relative percent difference values is $\sim 0.9\%$.

In conclusion, the line voltage dependent variability for the Thermo 81i unit was 0.4% or less at all three line voltages and concentrations studied. The variability for the MC-3000 at 105 V for 5 $\mu\text{g}/\text{m}^3$ was as high as 3.1%. The vendor informed us that the power supply used in that unit is rated for 110-140 V, which likely explains the variability observed at 105 V.

Table 28. Mercury Instruments MC-3000 Line Voltage Variation Data

Mercury Instr.02 MC-3000	Line VAC ($\pm 0.1V$)	80i 5-min avg. $\mu g/m^3$	Nested Rel. % Diff.
5.00 $\mu g/m^3$ Nominal	115.0	6.82	
	105.0	6.62	3.1%
	125.0	6.74	1.4%
	115.0	6.85	
	105.0	6.62	3.1%
	125.0	6.69	2.0%
	115.0	6.81	
	105.0	6.90	2.5%
	125.0	6.77	0.6%
15.00 $\mu g/m^3$ Nominal	115.0	6.65	
	115.0	19.95	
	105.0	20.01	0.07%
	125.0	20.05	0.1%
	115.0	20.10	
	105.0	19.89	0.6%
	125.0	19.85	0.8%
	115.0	19.92	
	105.0	19.95	0.2%
30.00 $\mu g/m^3$ Nominal	125.0	19.90	0.1%
	115.0	19.92	
	115.0	40.41	
	105.0	40.36	0.00%
	125.0	40.31	0.1%
	115.0	40.31	
	105.0	40.29	0.05%
	125.0	40.31	0.1%
	115.0	40.23	
	105.0	39.97	0.5%
	125.0	39.81	0.9%
	115.0	40.11	

Effect of External Temperature on Calibrator Output

To investigate the effect of external operating temperature on the mercury vapor concentration delivered by the calibrators, they were placed inside a Revco Model RTC30-99D Stability Test Chamber. A photo of the chamber is shown in Figure 33.

An inter-unit nesting procedure comparing the Thermo02 81i and the MC-3000 as test units vs. the Thermo03 81i as the control unit was used. The Thermo02 and MC-3000 units were placed simultaneously in the test chamber and operated at temperatures of 30°C, 20°C, and 10°C. Their Hg vapor concentrations were compared to those of the Thermo03 unit that was located on an adjacent lab bench at ambient laboratory temperature. Eight-minute intervals were used for the temperature studies. The concentration values for the two test calibrators were compared to the bracketed control calibrator, and nested ratios were calculated. The experimental sequence is the 3x3 matrix provided in Table 29.

Figure 33. Temperature Chamber

Table 29. Temperature 3x3 Experimental Matrix

30°C, 5 $\mu\text{g}/\text{m}^3$	20°C, 5 $\mu\text{g}/\text{m}^3$	10°C, 5 $\mu\text{g}/\text{m}^3$
30°C, 15 $\mu\text{g}/\text{m}^3$	20°C, 15 $\mu\text{g}/\text{m}^3$	10°C, 15 $\mu\text{g}/\text{m}^3$
30°C, 30 $\mu\text{g}/\text{m}^3$	20°C, 30 $\mu\text{g}/\text{m}^3$	10°C, 30 $\mu\text{g}/\text{m}^3$

The data for the 3x3 matrix are presented in Tables 30 and 31. The results highlighted with a light blue are nested ratios for the Thermo 81i, and results highlighted in light orange are nested ratios for the Mercury Instruments MC-3000. To determine the temperature effect on the Hg concentration delivered by the test calibrators, the nested ratios were subsequently compared. The nested ratio variation and average variation were calculated for each test calibrator at each concentration (blue and orange bold type, Table 31).

Table.30. Thermo 80i - 02 and Mercury Instruments MC 3000 Temperature Data at 20 and 30 °C.

30°C, 5.00 µg/m3 Nominal			20°C, 5.00 µg/m3 Nominal		
Reference Rovani WRI Notebook 1190 Page 109 (01/14/08)			Reference Rovani WRI Notebook 1190 Page 110 (01/15/08)		
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio	Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio
1 Thermo03 81i, ambient	4.89		1 Thermo03 81i, ambient	4.78	
2 Thermo02 81i, 30°C	4.73	0.968	2 Thermo02 81i, 20°C	4.77	0.998
3 Merc. Instr. MC-3000, 30°C	8.65	1.771	3 Merc. Instr. MC-3000, 20°C	6.62	1.385
4 Thermo03 81i, ambient	4.88		4 Thermo03 81i, ambient	4.78	
5 Thermo02 81i, 30°C	4.73	0.969	5 Thermo02 81i, 20°C	4.77	1.000
6 Merc. Instr. MC-3000, 30°C	8.64	1.770	6 Merc. Instr. MC-3000, 20°C	6.60	1.384
7 Thermo03 81i, ambient	4.88		7 Thermo03 81i, ambient	4.76	
8 Thermo02 81i, 30°C	4.73	0.970	8 Thermo02 81i, 20°C	4.77	1.001
9 Merc. Instr. MC-3000, 30°C	8.61	1.776	9 Merc. Instr. MC-3000, 20°C	6.60	1.385
10 Thermo03 81i, ambient	4.87		10 Thermo03 81i, ambient	4.77	
30°C, 15.00 µg/m3 Nominal			20°C, 15.00 µg/m3 Nominal		
Reference Rovani WRI Notebook 1190 Page 109 (01/14/08)			Reference Rovani WRI Notebook 1190 Page 111 (01/15/08)		
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio	Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio
1 Thermo03 81i, ambient	15.08		1 Thermo03 81i, ambient	14.92	
2 Thermo02 81i, 30°C	14.37	0.953	2 Thermo02 81i, 20°C	14.44	0.968
3 Merc. Instr. MC-3000, 30°C	19.95	1.323	3 Merc. Instr. MC-3000, 20°C	19.90	1.334
4 Thermo03 81i, ambient	15.08		4 Thermo03 81i, ambient	14.91	
5 Thermo02 81i, 30°C	14.35	0.952	5 Thermo02 81i, 20°C	14.45	0.969
6 Merc. Instr. MC-3000, 30°C	19.95	1.324	6 Merc. Instr. MC-3000, 20°C	19.91	1.336
7 Thermo03 81i, ambient	15.06		7 Thermo03 81i, ambient	14.90	
8 Thermo02 81i, 30°C	14.32	0.951	8 Thermo02 81i, 20°C	14.44	0.971
9 Merc. Instr. MC-3000, 30°C	19.98	1.327	9 Merc. Instr. MC-3000, 20°C	19.94	1.341
10 Thermo03 81i, ambient	15.05		10 Thermo03 81i, ambient	14.83	
30°C, 30.00 µg/m3 Nominal			20°C, 30.00 µg/m3 Nominal		
Reference Rovani WRI Notebook 1190 Page 110 (01/14/08)			Reference Rovani WRI Notebook 1190 Page 111 (01/15/08)		
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio	Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio
1 Thermo03 81i, ambient	30.59		1 Thermo03 81i, ambient	30.40	
2 Thermo02 81i, 30°C	28.68	0.940	2 Thermo02 81i, 20°C	28.40	0.937
3 Merc. Instr. MC-3000, 30°C	40.00	1.311	3 Merc. Instr. MC-3000, 20°C	40.16	1.325
4 Thermo03 81i, ambient	30.43		4 Thermo03 81i, ambient	30.22	
5 Thermo02 81i, 30°C	28.57	0.940	5 Thermo02 81i, 20°C	28.31	0.939
6 Merc. Instr. MC-3000, 30°C	40.03	1.317	6 Merc. Instr. MC-3000, 20°C	40.05	1.328
7 Thermo03 81i, ambient	30.35		7 Thermo03 81i, ambient	30.10	
8 Thermo02 81i, 30°C	28.51	0.940	8 Thermo02 81i, 20°C	28.22	0.938
9 Merc. Instr. MC-3000, 30°C	40.05	1.321	9 Merc. Instr. MC-3000, 20°C	40.25	1.339
10 Thermo03 81i, ambient	30.28		10 Thermo03 81i, ambient	30.04	

Table 31. Thermo 80i - 02 and Mercury Instruments MC 3000 Temperature Data at 10 °C.

10°C, 5.00 µg/m3 Nominal			Nested Ratio Variation	Average Variation
Reference Rovani WRI Notebook 1190 Page 111 (01/16/08)			(Max-Min) / Avg	at 5 µg/m3 Nominal
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio		
1 Thermo03 81i, ambient	4.79			
2 Thermo02 81i, 10°C	4.92	1.027	5.9%	
3 Merc. Instr. MC-3000, 10°C	6.50	1.357	27.5%	
4 Thermo03 81i, ambient	4.79			
5 Thermo02 81i, 10°C	4.93	1.030	6.1%	5.9%
6 Merc. Instr. MC-3000, 10°C	6.49	1.356	27.5%	27.6%
7 Thermo03 81i, ambient	4.78			
8 Thermo02 81i, 10°C	4.91	1.026	5.6%	
9 Merc. Instr. MC-3000, 10°C	6.49	1.356	27.9%	
10 Thermo03 81i, ambient	4.79			
10°C, 15.00 µg/m3 Nominal			Nested Ratio Variation	Average Variation
Reference Rovani WRI Notebook 1190 Page 112 (01/16/08)			(Max-Min) / Avg	at 15 µg/m3 Nominal
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio		
1 Thermo03 81i, ambient	14.85			
2 Thermo02 81i, 10°C	14.57	0.982	3.0%	
3 Merc. Instr. MC-3000, 10°C	19.58	1.319	1.1%	
4 Thermo03 81i, ambient	14.83			
5 Thermo02 81i, 10°C	14.53	0.980	2.9%	2.9%
6 Merc. Instr. MC-3000, 10°C	19.57	1.320	1.2%	1.3%
7 Thermo03 81i, ambient	14.82			
8 Thermo02 81i, 10°C	14.49	0.978	2.8%	
9 Merc. Instr. MC-3000, 10°C	19.57	1.321	1.5%	
10 Thermo03 81i, ambient	14.81			
10°C, 30.00 µg/m3 Nominal			Nested Ratio Variation	Average Variation
Reference Rovani WRI Notebook 1190 Page 112 (01/16/08)			(Max-Min) / Avg	at 30 µg/m3 Nominal
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio		
1 Thermo03 81i, ambient	29.98			
2 Thermo02 81i, 10°C	24.90	0.831	12.1%	
3 Merc. Instr. MC-3000, 10°C	19.46*			
4 Thermo03 81i, ambient	29.93			
5 Thermo02 81i, 10°C	24.58	0.823	13.0%	12.9%
6 Merc. Instr. MC-3000, 10°C	19.54*			
7 Thermo03 81i, ambient	29.83			
8 Thermo02 81i, 10°C	24.41	0.819	13.5%	
9 Merc. Instr. MC-3000, 10°C	19.89*			
10 Thermo03 81i, ambient	29.79			
* Highest Concentration That Could Be Achieved At 10°C				
10°C, 5.00 µg/m3 Nominal				
Reference Rovani WRI Notebook 1241 Page 2 (01/18/08)				
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio		
1 Thermo03 81i, ambient	4.74			
2 Thermo02 81i, 10°C	4.84	1.020		compare to above avg = 1.028
3 Thermo03 81i, ambient	4.75			
10°C, 15.00 µg/m3 Nominal				
Reference Rovani WRI Notebook 1241 Page 2 (01/18/08)				
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio		
1 Thermo03 81i, ambient	14.71			
2 Thermo02 81i, 10°C	13.68	0.931		compare to above avg = 0.980
3 Thermo03 81i, ambient	14.68			
10°C, 30.00 µg/m3 Nominal				
Reference Rovani WRI Notebook 1241 Page 2 (01/18/08)				
Calibrator and Temperature	80i 5-min avg, µg/m3	Nested Ratio		
1 Thermo03 81i, ambient	30.09			
2 Thermo02 81i, 10°C	23.88	0.796		
3 Thermo03 81i, ambient	29.88			
4 Thermo02 81i, 10°C	23.95	0.803		compare to above avg = 0.824
5 Thermo03 81i, ambient	29.77			
6 Thermo02 81i, 10°C	23.99	0.807		
7 Thermo03 81i, ambient	29.67			

The data reveal that there are two instances in which a particular temperature/concentration condition pushes the MC-3000 beyond its capability to generate a reliable Hg vapor source. These conditions are highlighted in Table 32.

Table 32. Mercury Instruments MC-3000 Failure Conditions

30°C, 5 µg/m ³	20°C, 5 µg/m ³	10°C, 5 µg/m ³
30°C, 15 µg/m ³	20°C, 15 µg/m ³	10°C, 15 µg/m ³
30°C, 30 µg/m ³	20°C, 30 µg/m ³	10°C, 30 µg/m ³

At a nominal setting of 5 µg/m³ at an ambient temperature of 30°C, the MC-3000 is delivering a Hg vapor concentration that is ~30% higher than at the other two temperatures. This calibrator uses a slightly below-ambient temperature Hg vapor condensation chamber that is adversely affected by high operating temperature. Although the unit's readout indicates that it is producing 5 µg/m³, the elevated temperature of the condensation cell is actually generating more Hg vapor than it should. Conversely, at a nominal setting of 30 µg/m³ at 10°C, the condensation chamber is too cold to be able to produce the required Hg vapor concentration. The upper concentration limit at 10°C is limited to ~20 µg/m³. Possibly the Peltier cooler in the condensation equilibrium chamber in this device is being taxed beyond its capabilities.

The data for the Thermo02 81i show a decrease in its delivered Hg concentration at the 30 µg/m³ setting at an operating temperature of 10°C (Table 33).

Table 33. Thermo Fisher 81i Failure Conditions

30°C, 5 µg/m ³	20°C, 5 µg/m ³	10°C, 5 µg/m ³
30°C, 15 µg/m ³	20°C, 15 µg/m ³	10°C, 15 µg/m ³
30°C, 30 µg/m ³	20°C, 30 µg/m ³	10°C, 30 µg/m ³

Part of the 10°C sequence was repeated to determine if the data were an anomaly or if the data could be replicated. These data are attached under the original 10 °C sequence. The data were replicated at all three concentrations. It appears that an operating temperature of 10 °C pushes the Thermo unit beyond its capability to reliably deliver Hg vapor at a concentration of 30 µg/m³.

From the temperature studies, it is apparent that neither vendor unit design can perform without significant variability within the full 10-30 °C temperature range. Possibly this is due to taxing the Peltier devices beyond their capabilities, and operating one or more of the mass flow controllers outside of their certified specification / calibration ranges at the extreme temperatures. The generator/calibrator units should be operated near ambient temperatures of 20 °C. This means that they must be housed and used in rooms with reasonable temperature control.

A Qualification acceptance requirement of steady operation between 10-30 °C appears to be unrealistic.

Effect of External Pressure on Generator/Calibrator Output

To investigate the effect of external (atmospheric) pressure on the calibrators, a new 55-gallon stainless steel drum with sealable lid was utilized as a pressure chamber. A photo of the pressure chamber is shown in Figure 34.

Figure 34. Pressure Chamber

Six ports were welded into the lid to accept stainless pipe thread and compression fittings. These include a pressure relief valve (top), electrical cord (mid left), PFA line from a compressed air cylinder for chamber pressurization (center), digital pressure indicator (mid right), PFA Hg output line to the analyzer (bottom left), and PFA clean dry air (CDA, bottom right) inlet to the calibrator in the chamber. A calibrator was placed inside the drum, the lid was sealed, and the calibrator was operated at ambient pressure and two hyperbaric conditions. The ambient barometric pressure in Laramie, WY is 0.78 atm, which served as the control pressure. The two hyperbaric conditions used were 0.95 atm and 1.1 atm. For operating this chamber at sea level, a mild vacuum can be applied to such a chamber to simulate high altitude conditions. The experimental sequence used was an inter-unit sequence in which the test calibrator was operated at 0.78, 0.95, and 1.1 atm with a return to 0.78 atm. Meanwhile, the control calibrator was operated at 0.78 atm on an adjacent lab bench. The effect on the Hg concentration delivered by the calibrators was evaluated at three nominal concentration settings. Eight-minute intervals

were used between readings. As with all other testing described in this report, 5-minute averages were used for the 80i analyzer results.

Using this experimental setup, three conditions of atmospheric pressure are applied only to the generator unit itself, and not to the inlet or outlet lines for air and calibration gas flow (the back pressure variability was evaluated in the experiments described earlier). This setup utilizes the Thermo 80i spectrometer and the control calibrator outside of the pressure chamber. Table 34 shows the experimental procedure that was conducted for the pressure studies.

Table 34. Matrix for 3x3 Ambient Pressure Studies

Thermo02 (test)	Thermo03 (control)	5 $\mu\text{g}/\text{m}^3$	Day 1	0.78, 0.95, 1.1, 0.78 atm
Thermo02 (test)	Thermo03 (control)	15 $\mu\text{g}/\text{m}^3$	Day 2	0.78, 0.95, 1.1, 0.78 atm
Thermo02 (test)	Thermo03 (control)	30 $\mu\text{g}/\text{m}^3$	Day 3	0.78, 0.95, 1.1, 0.78 atm
MC-3000 (test)	Thermo03 (control)	5 $\mu\text{g}/\text{m}^3$	Day 4	0.78, 0.95, 1.1, 0.78 atm
MC-3000 (test)	Thermo03 (control)	15 $\mu\text{g}/\text{m}^3$	Day 5	0.78, 0.95, 1.1, 0.78 atm
MC-3000 (test)	Thermo03 (control)	30 $\mu\text{g}/\text{m}^3$	Day 6	0.78, 0.95, 1.1, 0.78 atm

Results for concentrations of 5, 15, and 30 $\mu\text{g}/\text{m}^3$ are presented in Tables 35-37, respectively for the Thermo Fisher 81i 02 unit and Mercury Instruments MC-3000 unit, each nested against the Thermo Fisher 81i 03 unit.

In general, there is very little change in the nested ratios for the daily sequences for either the Thermo 81i or Mercury Instruments MC-3000 generator units, indicating that the effect of external pressure on the units is very small. Although there was an apparent anomaly in the data with the MC-3000 at 5 $\mu\text{g}/\text{m}^3$, initial 0.78 atm test data (nested ratio ~ 0.5 , Table 37), the later replicate final 0.78 data points are consistent with the pressurized data. Excluding the data set with the anomaly, the effect of external pressure on both units (as measured by the relative % differences of the nested ratios) is $\sim 2\%$ or less.

Although the effect of pressure changes on the calibrators was found to be minimal, at some point it might be useful to gauge the effects, if any, of atmospheric pressure changes on the entire calibrator/spectrometer system.

Table 35. Pressure Variation Data for Thermo 81i - 02 at 5 µg/m³ and 15 µg/m³

5 µg/m³ Nominal	Pressure, atm	5-min avg, µg/m³	Nested Ratio	Avg Nested Ratio	Rel % Difference vs. Avg Bracket
Thermo03 ambient		4.63			
Thermo02 ambient	0.773	4.49	0.973		
Thermo03 ambient		4.60			
Thermo02 ambient	0.775	4.47	0.970	0.970	
Thermo03 ambient		4.62			
Thermo02 ambient	0.776	4.47	0.969		
Thermo03 ambient		4.61			
Thermo03 ambient		4.61			
Thermo02 0.95 atm	0.958	4.49	0.974		
Thermo03 ambient		4.61			
Thermo02 0.95 atm	0.949	4.48	0.972	0.973	0.9%
Thermo03 ambient		4.61			
Thermo02 0.95 atm	0.959	4.49	0.974		
Thermo03 ambient		4.61			
Thermo03 ambient		4.61			
Thermo02 1.1 atm	1.086	4.49	0.975		
Thermo03 ambient		4.60			
Thermo02 1.1 atm	1.086	4.48	0.973	0.974	1.0%
Thermo03 ambient		4.61			
Thermo02 1.1 atm	1.086	4.49	0.974		
Thermo03 ambient		4.61			
Thermo03 ambient		4.60			
Thermo02 ambient	0.780	4.41	0.959		
Thermo03 ambient		4.60			
Thermo02 ambient	0.781	4.41	0.959	0.959	
Thermo03 ambient		4.60			
Thermo02 ambient	0.781	4.41	0.959		
Thermo03 ambient		4.60			
15 µg/m³ Nominal					
Thermo03 ambient		14.38			
Thermo02 ambient	0.770	13.52	0.941		
Thermo03 ambient		14.35			
Thermo02 ambient	0.771	13.49	0.940	0.941	
Thermo03 ambient		14.34			
Thermo02 ambient	0.773	13.48	0.940		
Thermo03 ambient		14.33			
Thermo03 ambient		14.31			
Thermo02 0.95 atm	0.947	13.54	0.946		
Thermo03 ambient		14.31			
Thermo02 0.95 atm	0.947	13.52	0.945	0.946	0.7%
Thermo03 ambient		14.31			
Thermo02 0.95 atm	0.951	13.52	0.946		
Thermo03 ambient		14.29			
Thermo03 ambient		14.27			
Thermo02 1.1 atm	1.087	13.57	0.951		
Thermo03 ambient		14.27			
Thermo02 1.1 atm	1.093	13.56	0.951	0.951	1.2%
Thermo03 ambient		14.26			
Thermo02 1.1 atm	1.092	13.55	0.951		
Thermo03 ambient		14.25			
Thermo03 ambient		14.26			
Thermo02 ambient	0.764	13.38	0.939		
Thermo03 ambient		14.23			
Thermo02 ambient	0.766	13.37	0.939	0.938	
Thermo03 ambient		14.24			
Thermo02 ambient	0.767	13.34	0.937		
Thermo03 ambient		14.25			

Table 36. Pressure Variation Data for Thermo 81i - 02 at 30 µg/m³ and Mercury Instruments MC-3000 at 5 µg/m³

30 µg/m ³ Nominal	Pressure, atm	5-min avg, µg/m ³	Nested Ratio	Avg Nested Ratio	Rel % Difference vs. Avg Bracket
Thermo03 ambient		28.99			
Thermo02 ambient	0.779	26.99	0.932		
Thermo03 ambient		28.91			
Thermo02 ambient	0.781	26.92	0.933	0.933	
Thermo03 ambient		28.83			
Thermo02 ambient	0.783	26.87	0.933		
Thermo03 ambient		28.77			
Thermo03 ambient		28.65			
Thermo02 0.95 atm	0.958	26.93	0.941		
Thermo03 ambient		28.56			
Thermo02 0.95 atm	0.953	26.90	0.942	0.941	1.1%
Thermo03 ambient		28.54			
Thermo02 0.95 atm	0.949	26.85	0.941		
Thermo03 ambient		28.55			
Thermo03 ambient		28.39			
Thermo02 1.1 atm	1.092	26.74	0.942		
Thermo03 ambient		28.38			
Thermo02 1.1 atm	1.089	26.71	0.942	0.941	1.1%
Thermo03 ambient		28.34			
Thermo02 1.1 atm	1.092	26.64	0.940		
Thermo03 ambient		28.34			
Thermo03 ambient		28.32			
Thermo02 ambient	0.773	26.27	0.928		
Thermo03 ambient		28.30			
Thermo02 ambient	0.774	26.25	0.928	0.928	
Thermo03 ambient		28.27			
Thermo02 ambient	0.775	26.27	0.929		
Thermo03 ambient		28.30			
5 µg/m³ Nominal					
Thermo03 ambient		4.51			
MC 3000 ambient	0.760	2.17	0.481		
Thermo03 ambient		4.51			
MC 3000 ambient	0.761	2.40	0.532	0.538	(anomaly value)
Thermo03 ambient		4.52			
MC 3000 ambient	0.761	2.72	0.601		
Thermo03 ambient		4.53			
Thermo03 ambient		4.54			
MC 3000 0.95 atm	0.953	7.11	1.570		
Thermo03 ambient		4.52			
MC 3000 0.95 atm	0.954	7.29	1.611	1.608	0.7%
Thermo03 ambient		4.53			
MC 3000 0.95 atm	0.948	7.43	1.644		
Thermo03 ambient		4.51			
Thermo03 ambient		4.52			
MC 3000 1.1 atm	1.105	7.34	1.626		
Thermo03 ambient		4.51			
MC 3000 1.1 atm	1.099	7.32	1.623	1.626	1.8%
Thermo03 ambient		4.51			
MC 3000 1.1 atm	1.094	7.36	1.630		
Thermo03 ambient		4.52			
Thermo03 ambient		4.52			
MC 3000 ambient	0.763	7.32	1.618		
Thermo03 ambient		4.53			
MC 3000 ambient	0.763	7.22	1.594	1.597	
Thermo03 ambient		4.53			
MC 3000 ambient	0.763	7.14	1.580		
Thermo03 ambient		4.51			

Table 37. Pressure Variation Data for Mercury Instruments MC-3000 at 15 $\mu\text{g}/\text{m}^3$ and 30 $\mu\text{g}/\text{m}^3$

15 $\mu\text{g}/\text{m}^3$ Nominal	Pressure, atm	5-min avg, $\mu\text{g}/\text{m}^3$	Nested Ratio	Avg Nested Ratio	Rel % Difference vs. Avg Bracket
Thermo03 ambient		13.91			
MC 3000 ambient	0.771	18.41	1.324		
Thermo03 ambient		13.90			
MC 3000 ambient	0.771	18.51	1.333	1.326	
Thermo03 ambient		13.88			
MC 3000 ambient	0.771	18.34	1.322		
Thermo03 ambient		13.87			
Thermo03 ambient		13.84			
MC 3000 0.95 atm	0.950	18.64	1.347		
Thermo03 ambient		13.84			
MC 3000 0.95 atm	0.955	18.20	1.316	1.331	0.3%
Thermo03 ambient		13.83			
MC 3000 0.95 atm	0.958	18.39	1.330		
Thermo03 ambient		13.83			
Thermo03 ambient		13.81			
MC 3000 1.1 atm	1.109	18.66	1.352		
Thermo03 ambient		13.80			
MC 3000 1.1 atm	1.102	18.78	1.361	1.356	2.1%
Thermo03 ambient		13.80			
MC 3000 1.1 atm	1.106	18.71	1.356		
Thermo03 ambient		13.79			
Thermo03 ambient		13.78			
MC 3000 ambient	0.770	18.07	1.310		
Thermo03 ambient		13.80			
MC 3000 ambient	0.770	18.55	1.344	1.329	
Thermo03 ambient		13.80			
MC 3000 ambient	0.770	18.40	1.333		
Thermo03 ambient		13.81			
30 $\mu\text{g}/\text{m}^3$ Nominal					
Thermo03 ambient		27.77			
MC 3000 ambient	0.764	36.70	1.324		
Thermo03 ambient		27.67			
MC 3000 ambient	0.763	37.15	1.343	1.341	
Thermo03 ambient		27.64			
MC 3000 ambient	0.763	37.47	1.356		
Thermo03 ambient		27.61			
Thermo03 ambient		27.56			
MC 3000 0.95 atm	0.958	37.24	1.352		
Thermo03 ambient		27.53			
MC 3000 0.95 atm	0.952	37.04	1.346	1.349	0.80%
Thermo03 ambient		27.52			
MC 3000 0.95 atm	0.956	37.11	1.350		
Thermo03 ambient		27.48			
Thermo03 ambient		27.44			
MC 3000 1.1 atm	1.111	36.66	1.336		
Thermo03 ambient		27.44			
MC 3000 1.1 atm	1.098	36.63	1.335	1.338	<0.1%
Thermo03 ambient		27.42			
MC 3000 1.1 atm	1.105	36.79	1.342		
Thermo03 ambient		27.42			
Thermo03 ambient		27.41			
MC 3000 ambient	0.763	36.95	1.349		
Thermo03 ambient		27.38			
MC 3000 ambient	0.763	36.03	1.316	1.336	
Thermo03 ambient		27.38			
MC 3000 ambient	0.764	36.77	1.343		
Thermo03 ambient		27.38			

CONCLUSIONS

Experimental procedures for conducting the qualification experiments outlined in the August 2007 EPA Interim Traceability Protocol were developed and optimized. The procedures were subsequently demonstrated with elemental mercury generators. The qualification test criteria to be established by EPA can be designed to be relatively simple, using a series of 3x3 matrices (3 mercury concentrations, 3 variable conditions) for each test. Candidate procedures were developed and demonstrated in the current study. Generator output was evaluated using three concentration settings: 5, 15, and 30 $\mu\text{g}/\text{m}^3$. Variables tested included back pressure, external pressure, temperature, and line voltage. Each of these variables was tested by using no more than three points. For back pressure, this was no pressure applied, and line restrictions corresponding to 5 psi and 9 psi back pressure. Umbilicals are not expected to cause greater than 9 psi back pressure. For atmospheric pressure, output was evaluated at 0.78 atm. (barometric pressure of Laramie, WY), 0.95 atm, and 1.1 atm. The temperatures evaluated were 10, 20, and 30 °C. Line voltages tested were 105, 115, and 125 volts. Results are summarized below.

1. The output of the generators is highly linear.
2. Identical model elemental mercury generator units from the same vendor do not necessarily provide identical concentration outputs at the same settings. It must be assumed that each one is unique relative to its linear calibration equation or individual monitoring points (for single point calibration).
3. The effect of back pressure that can be encountered due to long stack umbilicals, up to 9 psi, is relatively minor. Each vendor deals with back pressure differently.
4. The effect of external pressure is relatively minor.
5. The effect of temperature is significant. Components of the generators such as Peltier coolers and mass flow controllers can be adversely affected by temperatures ranging from 10 to 30 °C. Therefore the units should be operated in environments as close to 20 °C as possible.
6. The effect of line voltage between 105 – 125 V depends on the specification of the OEM power supplies selected by the vendors for use in their equipment. Some units are affected, others are not.
7. Limited experience with shipping elemental generator units has indicated that this could be an issue of significant concern. Experimental procedures should be implemented to document that generator output has not changed during shipping. Possibly generators should be certified at the locations where they will be used.

8. The qualification test criteria to be established by EPA can be designed to be relatively simple, using a series of 3x3 matrixes (3 concentrations, 3 variable conditions) for each test. The test procedures used for evaluating the effects of the variables described in the Qualification Experiments section of this report provide real-world results that can be used in the future design and implementation of EPA-defined qualification test procedures.

In addition, several other issues may need to be considered relative to overall CEM uncertainty. Analyzer stability and calibration drift over time needs to be studied further. CEM analyzer variability under the variety of conditions used for generator qualification is not well understood. Possible approaches for verifying generator performance in the field could include measurement of output by a portable analyzer, collection of calibration gas from a generator using a sorbent tube followed by analysis of the tube, or a nesting analysis against a certified calibration gas cylinder or reference generator. Our current focus is only on the elemental calibrators at this time. Oxidized mercury calibration systems will need to be evaluated and procedures for ensuring NIST traceability will need to be evaluated and developed.

REFERENCES

CRC Handbook of Chemistry and Physics, 2007-2008, 88th Edition, Taylor and Francis, NY., p. 6-142.

EPA, 2007, EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators, August.

Federal Register, May 18, 2005. EPA 40 CFR Parts 60, 72, and 75. Standards of performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units; Final Rule.

Huber, M.L., A. Laesecke, and D.G. Friend, 2006a. The Vapor Pressure of Mercury, NISTIR 6643.

Huber, M.L., A. Laesecke, and D.G. Friend, 2006b. Correlation for the Vapor Pressure of Mercury, Ind. Eng. Chem. Res. 45, 7351-7361.

Schabron, J.F., J.F. Rovani, Jr., and S.S. Sorini, 2007, Mercury CEM Calibration, WRI-07-R004 report to DOE under Cooperative Agreement DE-FC21-98FT40323, 2007.DOE Topical Report.