Adsorbent ("Sorbent") Tube Sampling of Gaseous Mercury Generator/Calibrators and Compressed Gaseous Mercury Cylinders

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REV.5

Hg CEMS should be routinely calibrated using NIST traceable calibration materials in order to provide reliable results. Mercury CEMS calibrations are conducted by using either gaseous mercury generator/calibrators ("calibrators"), permeation type devices (if applicable), or compressed gas cylinder mercury standards.

This document presents a methodology, loosely based on EPA Method 30B, for sampling and analyzing the output from gaseous mercury generator/calibrators devices, and compressed gas standards using adsorbent (sorben)t tubes. This methodology can be used for periodic field quality control checks of these devices, and for continuing stability checks of compressed gas standards.

Data quality objectives are identified in Section 5 of this method. In general, the data quality objectives are to minimize the error and bias associated with sorbent tube sampling so that comparisons with compressed calibration gases and mercury CEM "calibrators" provide meaningful data It is understood that the accuracy criteria in Method 30B is ±10%. It is expected that greater accuracy can be achieved by tightening the all around criteria found in the method. The goal of this methodology is to obtain results to within 5% accuracy.

1.0 SCOPE

1.1 This method employs an extractive system coupled with paired sorbent tubes to sample a slipstream of the output from the mercury generator/calibrator or cylinder.

1.2 An atmospheric vent is used so that little or no backpressure is present at the sorbent tube sample points. This is a very important aspect of this sampling and past anecdotal descriptions of data collected from sorbent tube sampling of mercury generators/calibrators have indicated numerous problems in acquiring matching data between the sorbent tubes and the expected output of the devices.

Note 1-1: Differences in CEM system set-up can differ between configurations used in the laboratory. Therefore it is important to ensure that the sorbent tube is sampling under atmospheric conditions and is not under pressure, nor pressurizing the calibration device.

1.3 The mercury generator/calibrators and cylinders are set to deliver concentrations based in ug/dscm, therefore, the flowrate and volume of the sample collected on the sorbent tube must be measured accurately to establish the theoretically sampled mass for comparing the analyses result to the expected generator/calibrator output.

1.4 The fundamental result will be a gravimetric catch of mercury as nanograms (ng). The flowrate will be in terms of cc/min or liters/min and the total volume collected on each sorbent tube will be in terms of liters. Dividing the gravimetric catch by the total sample volume will provide a concentration for comparing to the theoretical output of the generator or cylinder.

1.5 The objective of this method is to provide results to within 5% accuracy so that they can be used to determine whether the mercury generator/calibrator or cylinder is providing consistent calibration values for the CEM system.

1.6 It is recommended that at least 3 paired runs be performed; however, it is up to the user to determine how best to evaluate the calibration device or calibration gas for their quality assurance purposes.

2.0 REFERENCE DOCUMENTS

2.1 "EPA Traceability Protocol"
2.2 EPA Method 30B
2.3 40 CFR Part 75 Appendix K
2.4 EPA Method 1631 R-E

3.0 TERMINOLOGY

3.1 Atmospheric Vent – A colloquial term used to describe a sampling set-up designed to ensure no pressurization of the sample is occurring. An atmospheric vent in its simplest concept is where excess sample flow is vented to the atmosphere upstream of the sampling point.

3.2 Hg CEM System – The permanently installed mercury continuous monitoring system that employs mercury generator/calibrators/calibrators or calibration gases to conduct daily periodic calibrations and calibration checks.

3.3 Manifold – a series of connecting tubing and fittings to allow sampling of the mercury generator/calibrator or calibration gases using the sorbent tubes. The manifold has an atmospheric vent upstream of the sorbent tube sample point.

3.4 Mass Flow Meter/Controller – a device that is calibrated at the points of interest to adjust or control the flow of mercury calibration gas. These may also be used in the sorbent tube sample train.

3.5 Mercury generator/calibrator – a device that employs elemental mercury or ionic mercury and diluent gases to produce known concentrations of mercury vapor for calibrating mercury CEM systems. Permeation tubes may also be sampled using sorbent tubes so that their output concentrations may be checked.

3.6 NIST Traceable Ionic Mercury Solutions – Standard solutions of ionic mercury that are certified by NIST or that have NIST traceability.

3.7 Pump – a device used to acquire mercury generator/calibrator or calibration gas samples with sorbent tubes.

3.8 Percent Difference – The difference between the expected value of the mercury generator/calibrator or calibration gas and the results provided by the sorbent tube analyses.

3.9 PFA Teflon – Minimally reactive material similar for use in tubing and valves in the sampling manifold.

3.10 Relative Difference – The difference between the paired sorbent tube samples.

3.11 Slipstream – A colloquial term used to describe the sampling of a fractional amount of the total system flow. Sometimes referred to as "sub sampling".

3.12 Spiking – The application of a known amount of mercury onto a sorbent tube for conducting QA checks.

3.13 Thermal Analyses – Analyses of the carbon matrix of the sorbent tube by heating to 800C (or to manufacturer's specifications) with subsequent evolution of the trapped mercury and analyses by atomic adsorption, atomic fluorescence, or other appropriate spectroscopic technique.

3.14 Volume Totalizer – A meter used to measure the total sampled volume. The device must read out to three decimal places.

4.0 SUMMARY OF METHOD

4.1 Sampling – Effluent from the mercury generator/calibrator or compressed calibration gas is extracted via a slipstream using an atmospheric vent configuration at a nominal rate of 0.5 – 1.0 lpm. The rate depends on the size of the sorbent tube. Higher sampling rates may be used with the larger (10 mm) sorbent tubes, with the rate limiting factor being excessive mercury breakthrough from Section A to B of the tube.

Note 4-1: The flow meter should be calibrated at the exact flowrate (i.e., ±2%) to be used during sampling to minimize error. It is up to the end user to determine how best to conduct the calibrations and thus minimize error in this methodology. Calibrations of flow meters and totalizers are one means to accomplish this goal.

Note 4-2: The mercury generator/calibrator or compressed gas cylinder should be operated (to the extent practical) as it would be when used to calibrate the CEM system (i.e., generator effluent flowrate, temperature, etc is the same or similar for sampling as when calibrating the CEM system). Compressed gas cylinders should be sampled at the same flow rate used when calibrating the analyzer.

Note 4-3: The output concentration from the generator or cylinder is sampled for a duration so that a minimal theoretical gravimetric catch of 100 ng is captured on each sorbent tube. For example, if the generator or cylinder concentration is 1ug/dscm and the sample rate is 1.0 lpm, a sample time of 100 minutes is required to collect 100 ng. It is important to optimize sample rate with concentration to avoid overlong sample runs while capturing a mass that minimizes error at low loading.

Note 4-4: The minimum sample volume must also be met to minimize errors in this measurement. It is expected that at least 15 liters will be collected on each tube sample.

4.2 Analyses – The sorbent tube samples can be analyzed using conventional wet analyses (i.e., EPA Method 1631R-E or similar) or by thermal desorption combined with atomic adsorption, fluorescence or other appropriate spectroscopic technique.

In order to minimize error within the analyses, the calibration of the spectrometer should be held to a minimal range which brackets the expected sorbent tube catch. This may prove difficult when submitting samples to an analytical contract laboratory that generally calibrates over a wide range to capture the concentrations expected in their day to day samples. Independent checks of the instrument calibration must be conducted according to the analytical methods to minimize bias from the calibration.

For thermal desorption and on-site analyses, the range of the calibration curve should be tightly held around the expected concentration collected on the sorbent tubes. Even though the analytical technique is linear, this approach will minimize error to some extent. Method 30B criteria could be used to generate the calibration curve and to independently check the calibration; however in order to achieve the 5% accuracy goal, a tighter calibration and acceptance criteria should be used.

Note 4-5: For example, if one is testing mercury generator/calibrator output from concentration levels of 1 ug/dscm to10 ug/dscm, then a calibration curve having an appropriate ng level that brackets this range will tighten the linear fit, and thus produce less associated bias in the reported result. See Section 7.

4.3 Quality Assurance – Paired sorbent tube samples should be acquired at each concentration level of interest to determine precision of the analyses. A blank pair of samples should be acquired using the zero air at least once (for elemental mercury generator/calibrators only) to determine any background present. This may be eliminated if the CEM system/or analyzer can be used to verify zero mercury is present in the dilution side of the sampling system.

5.0 SIGNIGFICANCE AND USE

5.1 The sorbent tube sampling of mercury generator/calibrator output or calibration gases provides a gravimetric catch with corresponding volume to provide concentration based results.

5.2 The results are presented in units of ug/dscm.

Note 5-1: Standard units of pressure and temperature are 1 atmosphere and 20 ºC unless specifically stated otherwise.

5.3 The mercury generator/calibrator output or calibration gas value is of "known" concentration and the sorbent tube sampling and analyses is meant to be a quality assurance and quality control check of the known value between recertification.

5.4 This methodology can also be used as a means of spiking sorbent tubes for EPA Method 30B applications.

5.5 The data quality objectives are based on the concentration values of interest. At low concentration levels (e.g., < 5 ug/dscm) meeting a precision of 5% relative difference between the paired samples should be achievable. In practice relative differences have been observed to be in the 1-3% range.

5.6 Since the objective of this testing is to verify the output of mercury generator/calibrators and calibration gases, the error or bias of the individual

measurements is difficult to determine. There will be errors associated with the sampling and analyses of the sorbent tubes, and there will be errors associated with the output of the mercury generator/calibrator and calibration gases. Errors may cancel and they may also combine. Therefore, it is expected that for low concentration levels (e.g., < 5 ug/dscm) the maximum acceptable difference between the sorbent tube results and the mercury calibrators or calibration gases is 10% or 0.5 ug/dscm absolute.

Note 5-2: It is unknown what the actual data quality will be in practice as the procedures advocated in this method have not generally been applied to Appendix K or Method 30B sampling and analyses. It is likely that the precision and percent difference criteria can be tightened with application and use.

5.7 In general, the objective of this method is to minimize the error associated with sorbent tube sampling so that a valid assessment of the mercury generator/calibrator or calibration gas can be conducted. Sample collection and analyses can be highly technique driven and consistency between samples and sample runs is critical to achieving method precision. It is advisable that an experienced individual conduct the sampling and analyses (if thermal on-site analyses is performed) for all trial runs in a set to promote consistency.

6.0 APPARATUS

6.1 Sampling – The output of mercury generator/calibrator devices can be affected by back pressurization. Therefore, sampling must be conducted by sampling a slipstream of the effluent at or near atmospheric pressure. An atmospheric vent should be placed at the immediate outlet of the calibrator/generator, or upstream of the sample point. This will minimize pressurizing the sample exiting the generator device and avoid concentration changes in the output of the generator/calibrator. Depending on the output flowrate, another vent may be necessary at the sample point using a "T" configuration. A rotometer of other flow measurement device should be used to check that there is excess flow out the vent(s) when the sorbent tubes are sampling.

Note 6-1: The rotometer is used to check for excess flow, it should not be permanently installed on vent.

Note 6-2: Manufacturers have provided their recommended manifold configurations and these are presented as Addendums A and B to this method. A generic example of a manifold having an atmospheric vent sample port is also attached as Addendum C.

6.1.1 Connecting Tubing – PFA Teflon of sufficient length to connect from mercury generator/calibrator to manifold.

6.1.2 Tee or Cross – PFA Teflon (or SS for Hg^0) for connecting sorbent tube and atmospheric vent,

6.1.3 Mass Flow Meter/Controller – Calibrated at the exact values to be used to minimize error and bias. It is up to the user to determine the level of calibrations necessary – see note 4-1.

6.1.4 Volume Totalizer – Calibrated at the exact value to be used to minimize error and bias. It is up to the user to determine the level of calibrations necessary – see note 4-1.

6.1.5 Pump
6.1.6 Mercury Calibration Gas Regulators – Of appropriate materials.
6.1.7 Mercury Compressed Calibration Gases
6.1.8 Mercury generator/calibrator

6.2 Analyses – If performing thermal on-site analyses, consult the manufacturer's recommended list of components. In general, the instrumentation should be stand alone with its associated computer control and analyses software. Effluent should be properly vented to the atmosphere. The operator should allow the instrument to thermally equilibrate before performing instrument zeros, and calibration.

6.2.1 Calibration solutions – see Section 7.

7.0 REAGENTS

7.1 Ionic Mercury Solutions – NIST certified and in the concentration range of interest for the analyses. Concentration units are usually mg/mL – ug/mL.

Note 7-1: For on-site thermal analyses, an exact volume of an aqueous ionic mercury solution is applied to the carbon matrix and thermally desorbed and analyzed. Repetitions and dilutions produce a calibration curve through a specific mass range. This range should be held tightly so that the linear fit is more exact than when calibrating through a wide range. For example, a mass of 100 ng and 1000 ng is expected to be captured on the sorbent tube for two concentration levels of mercury generator/calibrator output. The thermal analyzer should be calibrated by selecting NIST traceable solutions that most closely approximate these mass loading when 50 – 100 ul of solution is applied during calibration.

Example 7-1: If the NIST ionic mercury solution had a concentration of 10 ug/mL (10 ng/ul), and 50 ul of solution were applied to the carbon matrix this would correspond to a mass loading of 50 ng. This mass plus the zero would constitute where the y-intercept would be placed in the calibration curve for the cited example. An upper level for the calibration curve could be established using a 15 ug/mL NIST traceable solution and applying 100 ul to the carbon matrix to result in a 1500 ng mass loading. The 50 ng to 1500 ng calibration points brackets expected catch of 100 ng to 1000 ng.

Alternately, two calibration curves could be prepared with one at the low range and one at the high range to reduce further the error associated with the analyses even though the calibration output is linear in nature. In any case, the calibration and analyses of sorbent tubes by thermal analyses and atomic adsorption spectroscopy is highly technique oriented. Analysts are encouraged to develop a specific set of procedures to unload the carbon from the traps, load the quartz vessels and place into the thermal chamber.

Independent checks of the calibration curve must be conducted using different solutions than used to prepare the original calibration. This procedure should identify if errors in the calibration curve exist so that they can be corrected while in the field.

A more detailed description of the thermal analytical requirements can be found in EPA Reference Method 30B.

8.0 HAZARDS

8.1 Mercury vapor is toxic. The output from the mercury generator/calibrator or calibration gas manifold system should be properly vented to the atmosphere without jeopardizing the integrity of the atmospheric vent system.

9.0 PROCEDURE

9.1 Pre-Test Preparations – Assemble the sampling manifold according to examples provided in Addendums A through C. Assure the manifold is leak free through the sorbent tubes. Turn on the mercury gas generator and allow equilibration of the internal components. Make sure the mercury is vented away from personnel.

9.2 Make the appropriate adjustments to the mercury generator/calibrator or compressed gas regulator and associated valving to ensure adequate flow for simultaneous sampling of two sorbent tubes with excess flow directed out the atmospheric vent. See manufacturer's recommendations for mercury generator/calibrator operation. In particular, ensure that 3/8" connecting tubing is used exiting the mercury generators/calibrators.

Note 9-1: The flow rate and conditions should be similar to those used when calibrating the Hg CEM system to the extent possible to evaluate the mercury generator/calibrator output under conditions of actual use.

9.3 Mercury Gas Manifold Equilibration – Allow the mercury from the generator or compressed gas to flow through the sampling manifold for a period of time sufficient to passivate the internal surfaces. The equilibration time is a function of the complexity of the manifold, materials of construction and the length of tubing. It is recommended that all components coming in contact with the mercury gas be of PFA Teflon construction. Stainless steel valves may be used for dry elemental samples.

Note 9-2. If evaluating the output of an oxidized mercury generator/calibrator special care should be taken to ensure all sampling system components are heated to 320ºF (from the exit of the device to the entrance of the sorbent tube). Stainless steel is not permitted in the sampling system components when sampling for oxidized mercury.

9.4 Attach the sorbent tubes to the sample manifold and begin to sample the generator or calibration gas. Ensure that all mass flow meters and volume totalizers are calibrated at the actual expected flow and volume to minimize bias and error of measurement. It is up to the end user to determine the level of calibration necessary. See Note 4-1. Insure that there is excess flow out the atmospheric vent.

Note 9-3: Sample for a time period sufficient to minimize error at low mass loadings, but not so long as to make for overly long sample periods. For example, a sample rate of 1-hr at 1.0 liters/minute at a concentration level of 3 ug/dscm will produce a nominal mass loading of 180 ng. The minimum mass to strive for to reduce error at low mass loadings is 100 ng and the minimum volume is 15 liters.

9.5 When the sample time is complete, turn off the pump, perform a leak check and immediately remove the sorbent tubes samples.

9.6 Record the following on a data sheet.

9.6.1 Mercury gas generator settings or mercury compressed gas standard certified value,

9.6.2 Sorbent tube ID,

9.6.3 Sorbent tube sample rate, sample time and sample volume.

9.7 Analyze the sample using either on-site thermal desorption combined with atomic adsorption spectroscopy or by sending the samples to an off-site laboratory.

9.8 Record the gravimetric catch and divide by the standard volume to convert to concentration.

10.0 CALCULATIONS

10.1 Precision – compare the results from the paired samples using the following equation:

(10-1) Absolute Value ((A-B)/(A+B)) = Relative Difference

The result must be 5% or less for the results to be meaningful. In practice, 1% is routinely achieved.

10.2 Breakthrough –Ensure that there is not breakthrough in the trap using the following equation:

(10-2) 100*(Section 2)/(Section 1) = Percent Breakthrough

The results should be less than 5%.

10.3 Comparison to Mercury generator/calibrator output or compressed calibration gas value – Compare the results on a mass loading basis to the expected results using the following equation:

(10-3) 100*((expected-observed)/expected) = Percent Difference

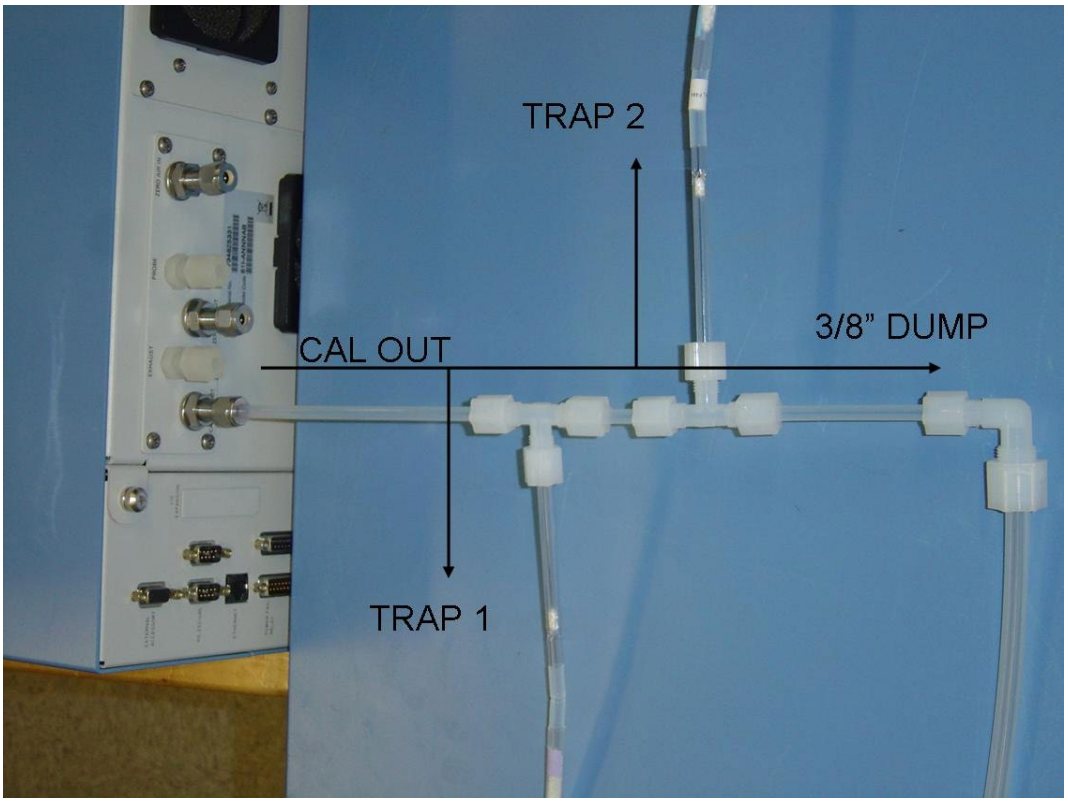
The results must be within 10% (or 0.2 ug/m3 absolute) to be of use in determining whether the generator or calibration gas is producing a reliable output.. The goal is to reduce error in both systems so that results closer to 5% are achieved.

11.0 REPORTING

11.1 Report all conditions from Section 9 and the results from the calculations contained in Section 10 of this document.

ADDENDUM A

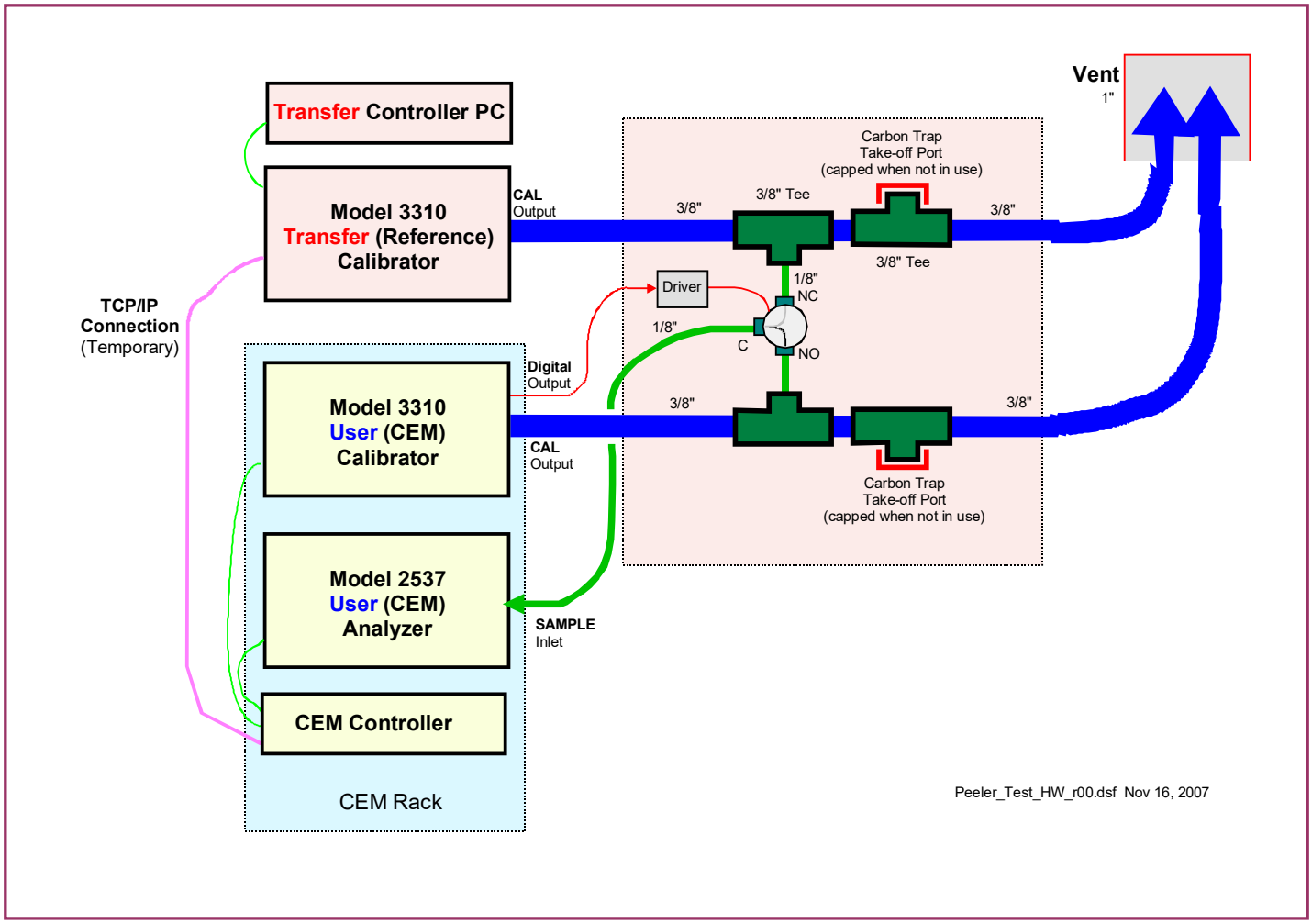
THERMO FISCHER SCIENTIFIC PROPOSED SAMPLE MANIFOLD



b

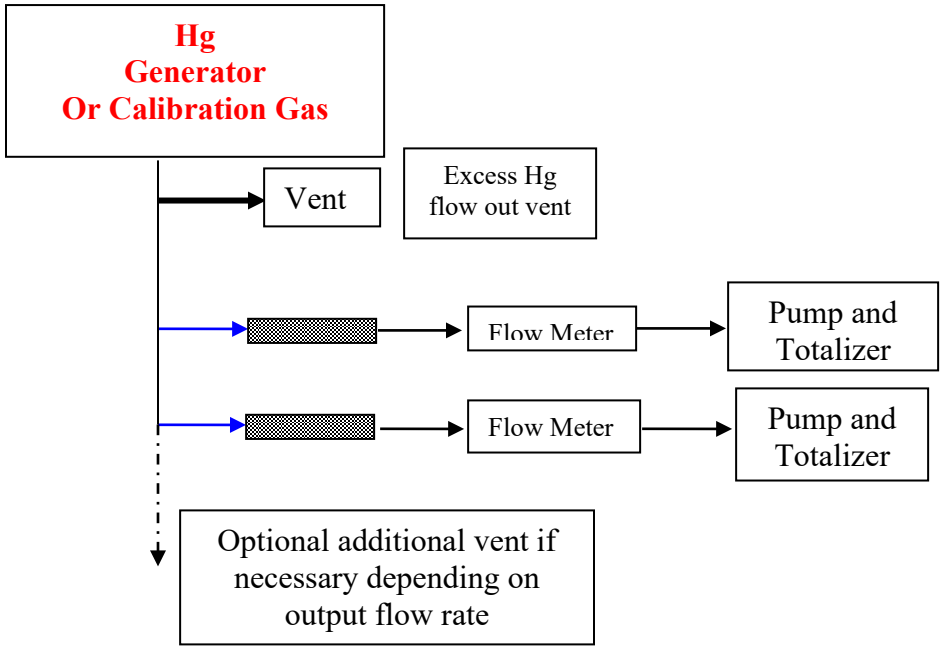
ADDENDUM B

TEKRAN PROPOSED SAMPLE MANIFOLD


Transfer Controller PC
Model 3310
Transfer (Reference)
Calibrator
CAL
Output
TCP/IP
Connection
(Temporary)
Model 3310
User (CEM)
Calibrator
Digital
Output
CAL
Output
Model 2537
User (CEM)
Analyzer
SAMPLE
Inlet
CEM Controller
CEM Rack
Vent
1"
Carbon Trap
Take-off Port
(capped when not in use)
3/8"
3/8" Tee
3/8"
3/8" Tee
Driver
1/8"
NC
1/8"
C
NO
3/8"
3/8"
Carbon Trap
Take-off Port
(capped when not in use)
Peeler_Test_HW_r00.dsf Nov 16, 2007

ADDENDUM C

GENERALIZED SAMPLE SET-UP


Hg
Generator
Or Calibration Gas
Vent
Excess Hg
flow out vent
Flow Meter
Pump and
Totalizer
Flow Meter
Pump and
Totalizer
Optional additional vent if
necessary depending on
output flow rate