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#### **Key Words**

- MATS
- MACT
- Mercury CEMS
- NIST-Traceability
- Mercury Traceability Protocol
- Permeation Source

# Introduction

The new Thermo Scientific<sup>™</sup> Model 84i mercury permeation source (Figure 1) provides a seamless quality control method for customers who are seeking to comply with the U.S. Environmental Protection Agency's (EPA) Utility Mercury and Air Toxics Standards (MATS), as well as the Maximum Achievable Control Technology (MACT) for mercury monitoring in cement production and industrial boilers. Industrial facilities that generate mercury gas and are using



**Figure 1:** Thermo Scientific Model 84i mercury permation source.

mercury continuous emissions monitoring systems (CEMS) are required by the EPA to have a NISTtraceable quality control method. The Model 84i permeation source is used to conduct quality control checks per the Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators in order to maintain NIST traceability. This new permeation source is an enhancement to the existing Thermo Scientific<sup>™</sup> Mercury Freedom System, offering customers a complete mercury monitoring solution with many advantages over conventional sorbent traps and field generators.



## Principle of Operation Overview

The Model 84i permeation source works by generating a specific and consistent concentration of mercury from a permeation assembly (Figure 2). The mercury permeation tube generates a known and reliable concentration of mercury at a constant

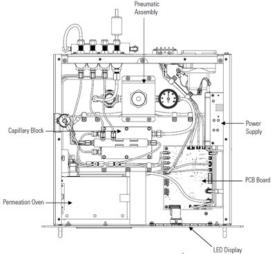


Figure 2: Scehmatic layout of the permeation assembly within the Model 84i permeation source.



temperature and flow. This generated mercury concentration is measured by the Thermo Scientific<sup>™</sup> Model 80i Mercury Analyzer and can be used to confirm the reliability of the Thermo Scientific<sup>™</sup> Model 81i Mercury Calibrator output in accordance with the Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators.

# **Permeation Oven**

The permeation rate of a permeation tube is highly dependent on the temperature. Having a stable temperature is the key to having a stable mercury output. The permeation oven has been designed in order to maintain a highly consistent temperature. Within the oven there are two thermistors, one controls the large thermal mass, while the other is used to control and maintain the actual gas temperaute within the oven. This temperature maintenance by the second thermistor ensures that a steady amount of mercury is transported to the Model 80i mercury analyzer. A fixed and continuous flow rate and tight control of the permeation oven temperature assures a repeatable and stable mercury concentration.

#### **Heated Capillary Block**

The heated capillary block maintains a consistent flow through the permeation oven. Internal capillaries receive zero air, which is supplied from the rear panel. Air flow through the first capillary leads into the permeation oven. The air flow through the second capillary acts as permeation dilution air and recombines with the mercury permeation air flow post permeation oven. The capillary block assembly is kept at a constant temperature. Also, the precision pressure regulator, located upstream in the pneumatic assembly, supplies the capillary block with air at a constant pressure. With constant temperature and pressure, both flow rates through each capillary remain constant, generating a stable and continuous mercury concentration.

# Advantages of Using a Mercury Permeation Source

To keep NIST traceability intact, periodic data quality evaluations of mercury calibrators need to be conducted at least once each calendar quarter. However, such evaluations should also be conducted after any malfunction, repair, or corrective action affects the calibrator's output, but does not necessitate recertification. Under the Interim EPA Traceability Protocol, there are four approved methods to quality check a mercury calibrator: field reference generator, permeation source, sorbent tube and mercury gas cylinder. While each method provides the same level of traceability, the permeation tube is a simple, reliable, and easy way to extend the certification of the Model 81i calibrator within the Mercury Freedom System. Though a field reference generator is certified using a more

rigorous protocol than those required for a user elemental mercury generator, it operates on a quarterly basis to check the mercury calibrator's performance and is time consuming. Like-wise the use of sorbent tubes for quality control is manually intensive without automation and must be done on a quarterly schedule to extend the calibrator certification. Quality checks done with elemental mercury compressed calibration gas cylinders require specially coated equipment and the output stability of the mercury cylinder must be checked. Extra precautions must also be taken if the analyzer used for the comparisons is sensitive to variation in the oxygen concentration in the sample gas. Comparisons can only be done if the oxygen concentrations in the compressed gas cylinder and in the mercury calibrator effluent are the same or are precisely known so that appropriate corrections can be applied.

The Model 84i permeation source requires monthly checks to maintain certification of the mercury calibrator, but is specifically designed to integrate into the industry standard Mercury Freedom System with distinct operational advantages. These advantages include quality checks that can be completely automated to confirm the output of the mercury calibrator. The quality checks can be set as the plant requires and can take place without interaction from plant personnel. Full system integration also provides a simple method to manually trigger an audit to either access additional audit data quickly and easily or aid in troubleshooting plant specific concerns. Permeation sources may require more frequent checks than field reference generators, sorbent tubes or mercury gas cylinders, but since the process is automated it requires little to no operator intervention. Traceability can be maintained if the quality assurance audits pass for up to a maximum of two years, at which time the mercury generator must be recertified (Figure 3).

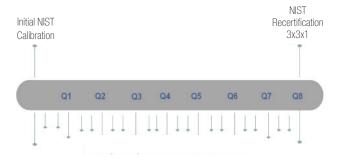


Figure 3: Monthly quality check with Model 84i permeation source.

## **Regulatory Requirements**

In order to maintain NIST traceability of a mercury source (i.e. Model 81i mercury calibrator), the unit must meet the Quality Assurance (QA) section of the Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators. Section 7 outlines the steps that must be taken to perform the QA audits, as well as the audit frequency and pass/fail criteria.

The NIST traceability of the Model 81i mercury calibrator may be extended up to two years if all QA audits pass the criteria each month. According to the protocol for QA checks done with a permeation source, the audit must be performed at least monthly, preferably weekly. The audit consists of a comparison between the mercury generator (Model 81i) and the permeation source (Model 84i). A typical data set indicating quality assurance is shown in Figure 4.

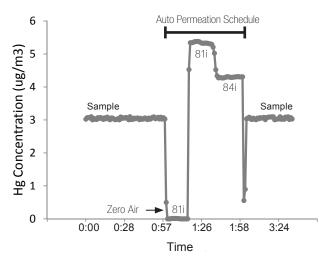
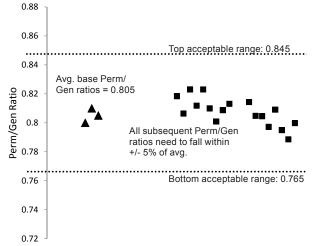


Figure 4: Representative data for quality assurance during an auto permation schedule.

During the automated permation schedule, three platues are prevelant: a zero response from the zero air from the Model 81i mercury generator, the mercury concentration generated from the Model 81i mercury generator, and the mercury concentration from the Model 84i permeation source. From this data set, the " $C_{perm}/C_{gen}$  ratio" (C is the respective concentration) is determined and compared to a base ratio, previously established. The performance of the mercury generator is acceptable if the value of the  $C_{perm}/C_{gen}$  ratio is within ±5.0% of the base ratio (Figure 5). For complete details on how to



**Figure 5:** Typical correlation between the average Base "Per/Gen" Ratio and all other Perm/Gen ratios.

maintain NIST traceability using a permeation source, see the Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators (http://www.epa.gov/ ttnemc01/metals/ElemHgProtocol.pdf).

# Integrating the Model 84i Permeation Source into a Mercury Freedom System

The permeation source has been designed to easily integrate into existing Mercury Freedom Systems. It mounts into a standard 19 inch rack and has a 3U height (5.25 inches) in order to accommodate racks systems that are already close to capacity (Figure 6). The permeation source connects to and is controlled by the Model 80i mercury analyzer via an RS-485 cable. Control of the source can be done either via the front panel of the Model 80i analyzer or through DAS connected to the analyzer. Once integrated in the system, the scheduled QC checks, via the analyzer's scheduled events or through the DAS, do not require any effort from employees unless the resulting tests detect a problem.



Figure 6: Thermo Scientific Mercury Freedom Continuous Emissions Monitoring System with Model 84i configuration.

In order to ensure the most consistent results between the comparison of the outputs of the Model 81i mercury calibrator and the Model 84i permeation source, the feed gas (either air or nitrogen) is supplied by a tee fitting that is placed in line with the inlet of the Model 81i mercury calibrator. The output of the permeation source is plumbed to the instrument span port of the Model 80i mercury analyzer. Once the Model 84i permeation source has been mounted, and connected electrically and pneumatically, the Model 80i mercury analyzer firmware will need to be updated in order to communicate with the Model 84i permeation source. This firmware is available on the On-line library.

#### Summary

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The Thermo Scientific Model 84i permeation source is the only instrument that is designed to fully integrate within the Thermo Scientific Mercury Freedom System. A single Model 84i permeation source can support two co-located Mercury Freedom Systems and trigger either automated or manual audits that confirm mercury calibrator performance or quickly and easily aid troubleshooting. As an approved method for meeting interim protocol QC requirement, the permeation source, with its exceptional stability and excellent precision, easily meets the U.S. EPA Utility MATS and Cement MACT regulatory requirements.

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