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Portable Mercury Detector Testing and Evaluation Report

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Executive Summary

The purpose of this project was to provide credible information on the selection and implementation of technologies to protect human health and the environment during a response and remediation effort following a spill or other release to the environment. This was achieved by testing and evaluating multiple monitors capable of detecting mercury (Hg) in the ambient air. Currently, these portable monitors are used by the EPA's emergency response on-scene coordinators (OSC) to characterize Hg spills and provide air monitoring data when clearing residential and commercial buildings after Hg cleanups. However, only one portable real-time monitor has been used for clearance to date because evaluations indicated only that monitor was able to provide equivalent results to the accepted integrated air sampling (sorbent tube) method. Hence, the primary objective of this study was to determine if additional portable monitors provided the sensitivity and accuracy to detect Hg concentrations in the air necessary for building re-occupancy.

Five commercially available portable Hg detectors from two vendors (Ametek Arizona Instrument LLC, Chandler, AZ, and Ohio Lumex, Solon, OH) were evaluated for their performance outputs against a National Institute of Standards and Technology (NIST) traceable saturated mercury vapor generated by a Tekran® Model 3310 Elemental Mercury Calibrator (Tekran Instruments Corporation, Toronto, Canada). The five Hg instruments evaluated were Ametek Arizona Instrument's Jerome® J405 and Jerome® J505 and Lumex's RA-915+, RA-915M, and Light 915. Because of multiple malfunctions with the operation of the Lumex Light 915, testing was not completed with this instrument.

Each detector's performance under controlled laboratory conditions was evaluated against EPA's Performance Specification (PS) 12A (US EPA, 2005), "Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Monitoring System in Stationary Sources." PS 12A specifies that a mercury instrument is accurate if its measurements are within 20% relative accuracy (RA) of the standard method used. While this PS is not directly applicable to portable Hg instruments, it does provide a metric for comparison that is appropriate under the laboratory testing conditions. Each of the mercury detection instruments was evaluated both with and without an interferent (ammonia, NH_3) for accuracy, precision, and linearity. It should be noted that integrated sorbent tube air samples actually collected in the field by EPA OSCs during a mercury cleanup must adhere to the Superfund Contract Laboratory Program (CLP) quality assurance/quality control requirements which may be less stringent than EPA PS 12A.

The primary objective of the Hg detector testing was to determine if the instruments could accurately detect Hg concentrations in the air below the Centers for Disease Control and Prevention's Agency for Toxic Substances and Disease Registry (ATSDR) recommended action level (clearance) of 1 $\mu g/m^3$ for normal residential occupancy (ATSDR, 2012). The performance of each of these instruments is summarized below.

In summary, the Jerome® J505 and both the Lumex-RA 915 M and Lumex-RA 915+ instruments were found to be compliant with EPA PS 12A, for Hg concentrations under 28.01 $\mu g/m^3$ and can be used to accurately characterize Hg contamination or provide clearance for an indoor location. These instruments were observed to meet the detection and sensitivity requirements for assisting with a clearance determination based on the 1 µg/m^3 residential action level (US EPA, 2019). However, the Jerome® J405 was less sensitive, with no detector responses observed for target Hg concentrations below 1.10 µg/m^3 and therefore was not in compliance with EPA PS 12A. Additionally, the Lumex detectors had response times within a few seconds (2 to 7 seconds), whereas the Jerome® J505 response times were measured in minutes (2 to 6 minutes), independent of the environmental conditions or the presence of NH_3-interferent. These response readiness times were based on both ambient and cold storage test conditions and present an instrument-readiness caveat that users should be aware of. However, for Hg clearance purposes, a response time in either seconds or minutes is likely not a concern.

Jerome® J405. For relatively low temperature and relative humidity (RH) conditions (10 ˚C, 19% RH, and 23 ˚C, 30% RH), no detector responses were observed for target Hg concentrations below 1.10 µg/m^3. Note that these concentrations were near the minimum of the manufacturer's listed detection range of 0.5 to 999 µg/m^3 (ABLE Instruments & Controls, 2008).

Increases in temperature and RH (35 ˚C, 60% RH) resulted in a marked effect on the sensitivity of the instrument, decreasing the level of the observed detection limit from 1.10 µg/m^3 to 0.25 µg/m^3. A significant increase in accuracy occurred as the challenge concentration increased from 1.10 µg/m^3 (66.7% RA) to 17. 1 µg/m^3 (6.22% RA). The detector's response was found to comply with EPA's PS 12A for Hg concentrations ranging from 17.1 to 28.0 µg/m^3. The linearity of this instrument was found to be acceptable (R^2 >0.99) for concentrations greater than 1.10 µg/m^3, with a systematic bias of greater than 22%. The limit of detection (LOD) was not calculated for this instrument since no response was detected for Hg concentrations lower than 1.10 µg/m^3, and no measurements were made between 1.10 and 5.00 µg/m^3. The precision of the Jerome J405 was observed to increase as the challenge concentration increased from 0.25 µg/m^3 (relative standard deviation [RSD] = 55%) to 28.0 µg/m^3 (RSD = 0.95%).

Jerome® J505. This detector outperformed the J405 in terms of sensitivity, with an observed detector response at 0.25 µg/m^3 for all tested operating conditions. Moreover, the J505 was found to be compliant with EPA PS 12A and can be considered accurate for the Hg target range between 0.0 to 28.0 µg/m^3. Although an increase in temperature (up to 35 ˚C) and RH (60%) reduced the accuracy of the instrument, it was still in compliance with the EPA's performance specifications for accuracy. The response times of the Jerome® J505 were measured in minutes and response time doubled following cold storage.

The Jerome J505 exhibited a slope near a value of 1 (> 0.97), with relatively good linearity (R^2 >0.99) for Hg concentrations between 0 and 28.0 µg/m^3. The calculated LOD, based on instrument response-residuals when no Hg was introduced, was equal to 0.07 µg/m^3. The precision was also increased from the lowest target Hg concentration (0.25 µg/m^3, RSD = 17%) to the highest target concentration (28.0 µg/m^3, RSD = 0.45%).

Lumex-RA 915 M and Lumex-RA 915+. No significant differences were observed for either accuracy or precision in a comparison of the Lumex-RA 915+ and the Lumex-RA 915M for all target Hg concentrations tested. Both instruments were found to be compliant with EPA's performance specifications for Hg continuous emission measurements for two of the tested environmental conditions (10 ˚C, 19% RH, and 23 ˚C, 30% RH). Increasing the temperature and RH (to 35 ˚C and 60% RH) affected the performance of the instrument, with an RA at or greater than 20%.

Both the 915M and 915+ Lumex detectors exhibited similar slopes (0.91- 0.93) that tended to slightly underestimate the value of the Hg concentration of the Tekran calibrator. The linearity of the two detectors ($0.96 > R^2 > 0.98$) and their calculated LODs (< 0.002 µg/m^3) were also similar. The similarity in the findings are not surprising since the RA-915M is an updated version of the RA-915+, with a similar engineering design but including some additional features such as a lightweight outer casing, a built-in backlit screen display, an automated calibration test cell, and a USB cable connection.

The precision of both instruments was very good for the range of Hg concentrations evaluated in this study, with a less than 1.7% RSD for an Hg challenge concentration greater than 0.50 µg/m^3.

All of the detectors' response times were evaluated to determine the time required for readiness, accuracy, and speed after the instrument is powered on after being stored in a cold environment (≈ 5 °C) and in a warmer environment (24 °C). Both the Jerome J405, which uses a gold film sensor technology, and, to a lesser extent the Lumex RA-915M, which uses atomic absorption spectrometry at 254 nm with Zeeman correction for background absorption for interference-free measurement, produced rapid ready-time responses of 2 to 3 seconds and 5 to 7 seconds, respectively, independent of the environmental conditions. However, the J505, which uses atomic fluorescence spectroscopy, produced measured ready-time responses in minutes (2.7 minutes) rather than seconds at 24 °C, and the time was more than doubled (6.2 min) when it was used following overnight cold storage at $\underline{\approx}$ 5 °C to 4.6 °C. In addition, the Jerome units have the option to save and transfer test data via a USB connection, and the Lumex-RA 915M has an option to connect to a computer, whereas the Lumex RA-915+ does not have either of these options.

To determine the interference of an NH_3-containing gas stream with the instruments' performance, a gas mixture containing NH_3 (7.863 ppm sulfur hexafluoride, 514.9 ppm ammonia, and balance nitrogen) was introduced downstream of the Tekran® and RH equipment. The target environmental conditions for the interference evaluations were 23 °C and 30% RH. Interference evaluations were performed for the J405, J505, RA-915M, and RA-915+ detectors. The overall results indicate that none of the detectors' responses were affected by the presence of the NH_3 interferent at the target challenge concentrations (0.0 µg/m^3 and 4.70 µg/m^3).

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Acronyms and Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry
˚C	degrees Celsius
CESER	Center for Environmental Solutions & Emergency Response
DAS	data acquisition system
dscm	dry standard cubic meter
DQI	Data quality indicators
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectroscopy
ERTG	Emergency Response Technical Group
HSMMD	Homeland Security & Materials Management Division
HSRP	Homeland Security Research Program
L	Liter
LOD	Limit of detection
Hg	Mercury
$\mu g/m^3$	micrograms per cubic meter
MDL	method detection limit
m	Meter
min	Minutes
mL	Milliliter
ng/m^3	nanograms per cubic meter
NH_3	Ammonia
NIST	National Institute of Standards and Technology
OSC	On-Scene Coordinator
ppm	parts per million
QC	quality control
RA	relative accuracy
RH	relative humidity
RPD	Relative percent difference
RSD	relative standard deviation
T	temperature
SHEM	Safety, Health and Environmental Management

1. Project Description and Objectives

The U.S. Environmental Protection Agency's (EPA's) Homeland Security Research Program (HSRP) provides credible information that is used to protect human health and the environment from adverse impacts arising from terrorist threats and other contamination incidents. Within the HSRP, the Center for Environmental Solutions & Emergency Response (CESER), Homeland Security & Materials Management Division (HSMMD) conducts research to provide expertise and guidance on the selection and implementation of decontamination methods that may lead to significant reductions in the time and cost of wide area remediation efforts.

EPA's HSMMD research and technical expertise supports EPA's regional on-scene coordinators (OSCs) and response teams, as well as state and local emergency response agencies. As part of this support, HSMMD recently evaluated technologies to address indoor mercury (Hg) measurement and monitoring needs. Reliable real-time portable Hg detectors are integral to the OSCs and provide an agreed-upon alternative (ATSDR, 2012) to integrated area air sampling using sorbent tubes (US EPA, 2012) to assess indoor Hg contamination as well as to permit re-occupancy of a building following a Hg contamination incident. The current use of a real-time portable monitor for clearance sampling was based on an extensive comparison of portable monitor readings over 8 hours with NIOSH 6009 sorbent tube sampling results from samples collected over the same 8-hour time period in the same location. The testing specified in this document is part of HSMMD's efforts to identify and verify the performance of existing portable chemical detectors to detect Hg in air.

1.1 Purpose

Responding to an accident, fire, or deliberate chemical release can potentially expose first responders to harmful levels of toxic or corrosive chemicals. Additionally, following a contaminant release indoors, it is essential to protect the public health and provide a clearance determination following cleanup efforts. To minimize such exposures, first responders and emergency management professionals need reliable, sensitive, and portable monitoring devices that can rapidly indicate the presence of chemical hazards. The purpose of this work was to test and evaluate multiple Hg detectors that can detect Hg in the ambient air. These portable monitors are used by the EPA OSC community to obtain data for contamination screening and/or clearing residential and commercial buildings after Hg cleanups, depending on the measurement range of the instrument. All parties involved in a cleanup must agree to the use of portable monitors for clearance sampling. for This project purpose was to determine which instruments meet the detection and sensitivity requirements for assisting with a clearance determination using the ATSDR recommended action level of 1 $\mu g/m^3$ (ATSDR, 2012).

1.2 Objective

This report summarizes a project that evaluated the performance and operational characteristics of five portable Hg monitors. Specifically, the accuracy, precision, and interference effects from ammonia (NH_3) were evaluated for each Hg monitor. Additional interferents such as VOCs were identified but were not able to be tested at this time due to project constraints.

The overall objective was to provide the Emergency Response Technical Group (ERTG) with objective data on the performance of the portable Hg monitors that could be used for clearance sampling following a mercury release to the environment (indoors or outdoors). Previous comparisons were made between real-time portable instruments and the NIOSH 6009 sorbent tube method (Singhvi et al, 2001, 2003). Based on the results from these comparative studies, EPA and ATSDR came to an agreement that EPA OSCs could use the Ohio Lumex 915+ instrument for clearance sampling if specified criteria were followed.

1.3 Experimental Design

Portable Hg detectors developed by Ohio Lumex (Cleveland, OH) and AMETEK Arizona Instruments (Chandler, AZ) were evaluated for accuracy, precision, and linearity during exposure to varying environmental conditions and interferences. Detector sensors were exposed to a range of elemental Hg vapor concentrations at targeted relative humidity (RH) and temperature (mercury vapor and external) conditions. All target Hg gases were produced by a Hg generator (Tekran® Model 3310 Elemental Mercury Calibrator, Tekran Instrument Corporation, Knoxville, TN) that generates concentrations of mercury by using NIST-traceable saturated mercury vapor. The design was intended to evaluate the operation of the detectors in the variable temperature and RH environments that would be encountered in the field in different parts of the world throughout different seasons.

The following input/output characteristics were evaluated for each detector:

- **Calibration**

A seven-point calibration curve over the dynamic range was constructed by using varying Hg vapor concentrations while the temperature and RH were held constant. The objective of constructing the calibration range was to determine the lower and upper measurement limits for each sensor using the signal output range. The lower limit was defined as the minimum input Hg concentration that would cause a detector output that exceeded three times the signal-to-noise ratio of the sensor when Hg was not present. The upper limit of the range was defined as the maximum concentration at which the linearity of the calibration curve was not compromised. For these tests, the lower limit of each instrument was of higher importance for clearing a building, so the focus of the calibration curve was on the lower end of instrument sensitivity.

- **Relative Accuracy (RA)**

The RA (%) is defined by EPA Performance Specification 12A (US EPA, 2005) as the absolute mean difference between the mean Hg concentrations determined by the Hg detectors and the value determined by the reference method (RM) plus the 2.5% error confidence coefficient of the detector measurement series divided by the mean of the RM reference method tests. The calculation of RA (%) is described in the following equations:

$$RA\ (\%) = \frac{(|\bar{d}|+|CC|)}{\overline{RM}} \times 100 \quad (1)$$

where $|\bar{d}|$ is the absolute mean difference between the mean Hg detector responses (μg/m^3) and the actual input concentration:

$$|\bar{d}| = \frac{\sum_0^n RM - X_n}{n} \qquad (2)$$

For this project, the RM tests consisted of the set concentration input of the Tekran® Model 3310 calibrator, where X is the instrument response, n is the number of measurements, and CC is the 2.5 percent error confidence coefficient (one-tailed), calculated as follows:

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \qquad (3)$$

where S_d is the standard deviation, and t is the probability distribution.

- **Relative Percent Difference (RPD)**

The RPD (%) is used to determine whether the instrument is over- or under-reporting the concentration as compared to the RM. It is calculated as follows:

$$RPD\ (\%) = \frac{d}{RM} \times 100 \quad (4)$$

- **Precision**

Precision is expressed as the relative standard deviation (RSD) (%) of the measurements at each measurement point when steady state has been reached:

$$RSD = 100 \times \frac{S_d}{|d|} \quad (5)$$

- **Limit of Detection (LOD)**

If the detector's response (y) is linearly related to the set concentration input of the Tekran® Model 3310 calibrator's standard concentration (*x*), the calibration curve for each detector can be expressed as:

$$y = bx + a \quad (4)$$

Where a and b are the calibration curve intercept and slope, respectively.

The LOD can be expressed as:

$$LOD = \frac{3\, S_a}{b} \qquad (4)$$

where *Sa* is the standard deviation of the detector response of *y*-residuals when no Hg is generated by the Tekran® Model 3310 calibrator.

- **Cold Start Evaluation**

Response situations may not allow the time for instruments to warm up that would be available if operated in a laboratory setting. Monitoring instruments may need to provide full operational capabilities rapidly. Consequently, the portable Hg detectors were tested for the delay in time between turning the instrument on and its readiness for hazard detection, and for the accuracy and speed of response under such use. The speed for these capabilities was determined under two separate startup conditions: (1) for an overnight startup from room temperature and (2) after 24 hours in cold storage.

- **Interference Effects**

In emergency response situations, the local air may contain chemical compounds or mixtures that, although relatively innocuous, may mask or alter the response of a portable Hg detector. Examples of such potential interferences may be cleaning supplies, paint vapors, cat urine, or vehicle exhaust. The effect of potential interferences was assessed because such compounds can potentially produce two types of errors with the portable detectors: (1) erroneous reporting of the presence of Hg when none is present (false positives, FP) or (2) reduction in sensitivity or masking of response to Hg (false negatives, FN). The former error can waste time and resources in responding to an emergency; the latter error can expose responding personnel and the public to hazardous conditions.

Interference testing was performed by introducing a gas mixture containing ammonia (NH_3) (7.863 ppm sulfur hexafluoride, 514.9 ppm ammonia, and balance nitrogen) downstream of the Hg vapor generator and RH equipment. The target NH_3 concentration was the odor threshold of 8 to 10 ppm. The performance parameters that were investigated during interference testing are listed in Table 1-1.

Table 1-1. List of the Performance Parameters

Parameter	Objective	Basis of Comparison
Calibration	Determine usable range and linearity of detector	Detector readings at various concentrations of Hg challenge
Accuracy	Characterize agreement of detector readings with reference results	Compare detector readings to known Hg concentration or reference method results
Temperature and RH Effects	Evaluate effect of temperature and RH on detector performance	Target Hg challenges at different temperature and RH conditions
Cold Start Behavior	Evaluate effect of storage temperature on detector performance at startup	Compare response/recovery times, repeatability, and accuracy, after startup from cold storage
Interference Effects	Evaluate effect of contaminants that may interfere with detector performance	Sample interferents in clean air and along with target Hg concentration

1.4 Test Matrix

A series of tests were performed at increasing temperatures and RH parameters to simulate a range of real-world operating environment conditions consisting of humid, dry, hot, and cold conditions. The tested environmental conditions (Table 1-2) were 10 °C and 19% RH, 23 °C and 30% RH, and 35 °C and 60% RH. Some more extreme target conditions, such as 35 °C and 80% RH, were attempted, but could not be reached and maintained because of limited resources in controlling the RH at such levels.

For each test, the room temperature (environmental chamber) was maintained at the same temperature as the conditioned challenge gas.

Table 1-2. Tested Environmental Conditions

Environmental Condition	Target Hg Vapor and Room Temperatures (°C)	Target Hg Vapor RH (%)
A	10	19
B	23	30
C	35	60

The portable detectors were exposed to seven Hg concentrations at each of the three environmental conditions listed in Table 1-3, totaling 21 tests. Hg setpoints that were pre-programmed in the Tekran calibrator and previously verified by an independent sampling method were selected for evaluation. The Hg vapor concentrations in micrograms per cubic meter (µg/m^3) are listed in Table 2-2. The primary goal of this testing was to evaluate detector performance at low concentrations at or below the current EPA clearance level for residential buildings of 1 µg/m^3 to determine whether detectors other than the Lumex 915+ could be used for clearance sampling by EPA's OSCs.

Additionally, the effect of interferences that might mask or alter the response of a portable Hg detector were evaluated. The test matrix originally included interference effects from volatile organic compounds (VOCs) and ammonia; however, due to constraints of time and gas availability, interference testing was limited to ammonia, as shown in Table 1-4. Ammonia was deemed more likely to be found in indoor environments and as such, was prioritized first in the interference tests.

Table 1-3. Test Target Hg Concentrations

Level	Generated Hg Vapor Concentration (µg/m^3)
1	0.000
2	0.250
3	0.501
4	1.100
5	4.700
6	17.110
7	28.012

Table 1-4. Interference Test Target Conditions

Test	Generated Hg Vapor Concentration (µg/m^3)	Presence of NH_3 (8 ppm)
1	0.000	N
2	0.000	Y
3[a]	0.250	Y
4[a]	0.501	Y
5	1.100	Y
6[b]	4.700	N
7[b]	4.700	Y

[a] Test not performed with Lumex915 M, Lumex 915+, Jerome J405, or Jerome J505

[b] Test not performed with Lumex 915 Light

2. Material and Methods

This section describes the experimental testing and materials, including the portable Hg detectors, Hg generator, and the Fourier Transform Infrared Spectroscopy (FTIR) equipment used for interference measurements.

2.1 Bench-Scale Testing Setup

The bench scale testing setup is shown in Figure 2-1. It consisted of the Tekran Hg calibration system, a control chamber that provided a temperature-controlled environment to house the sample tubing and the sampling manifold, the portable Hg detectors, a humidification system, and an interferent loop with a digital mass flow controller. The entire setup was housed within a temperature-controlled environmental test chamber, which was maintained at the target operating temperature.

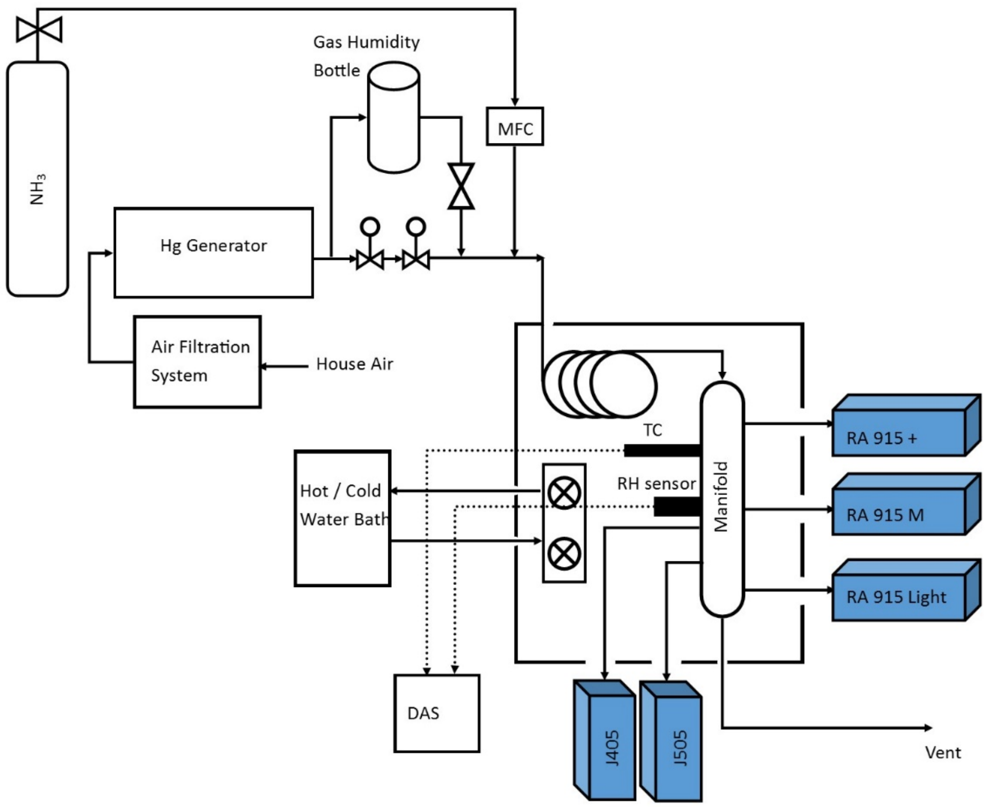


Figure 2-1: Bench-Scale Testing Setup

A slipstream of the dry Hg vapor generated by the Tekran calibrator was humidified to the target RH using a heated, high-flow gas humidity bottle (Fuel Cell Technologies, Inc., Albuquerque, NM). For the interference tests using NH_3, a second slipstream from the Hg generator was used to introduce the gas interferent (NH_3) to the bulk flow just after the split streams were rejoined. A digital mass flow controller (Smart Trak100, Sierra Instruments, Inc., Monterey, CA) was used to control the flow rate of the interferent gas to the bulk flow that was introduced into the gas manifold inside the temperature-controlled chamber. Once inside the chamber, the bulk flow traveled through a 10-foot length of sample tubing for additional mixing and temperature adjustment before entering the sampling manifold.

The temperature within the sampling manifold was measured using a standard K-Type thermocouple, and the RH was measured with a digital temperature/RH probe (HMP60. Vaisala, Helsinki, Finland). The intake air hose for each of the Lumex detectors was passed through pre-drilled openings located on the front side of the control chamber and connected to the sampling manifold. Quarter-inch sample tubing was used to connect the Jerome detectors to the sampling manifold. The entire length of each intake air hose and the quarter-inch sample tubing was maintained inside the control chamber. Although the detectors were maintained outside the control chamber, they were positioned against the outer walls in a manner that prevented exposure of the intake hoses and quarter-inch sample lines.

The control chamber provided a temperature-controlled environment to house the sample tubing and the sampling manifold. The temperature-controlled chamber consisted of a modified Rubbermaid 48-quart chest cooler (Newell Brands Inc., Atlanta, GA). Two 3/8” tubes (a supply and return) were installed in the back of the chamber to circulate the temperature-controlled water through a 240-mm water-regulated row heat exchanger with two computer fans, attached to promote air circulation over the radiator coils. The temperature-controlled water that flowed through the heat exchanger was conditioned and pumped by a refrigerating circulator (Isotemp 30165, Fisher Scientific, Waltham, MA, USA).

2.2 Hg Generation/Calibration System

All target Hg gases were generated by a Tekran® Model 3310 Elemental Mercury Calibrator (Figure 2-2). The Hg calibrator allows high-level Hg monitoring systems to be accurately calibrated using elemental Hg. The Model 3310 allows both multi-point calibrations and standard additions to be automatically initiated. The unit generates known Hg concentrations using a NIST-traceable temperature-controlled saturated Hg vapor source. According to the manufacturer, the chamber of the instrument contains 1 mL of mercury (13.5 g) immobilized on a proprietary sorbent bed of high surface area. The equilibration chamber temperature is controlled from 5 ºC to 50 ºC using an oven. The flow of nitrogen or dry air through the chamber is controlled by a digital mass flow controller. The nitrogen or dry air exiting the chamber is saturated with mercury vapor, and this stream is diluted with nitrogen or dry air into the concentration range of interest. The output concentration is controlled by setting the flow rates. The unit also generates a mercury-free zero flow so that blank measurements can be performed.

Figure 2-2. Tekran Model 3310

Hg concentrations of 0.00 μg/m^3 (zero-air), 0.250 μg/m^3, 0.501 μg/m^3, 1.100 μg/m^3, 4.700 μg/m^3, 17.110 μg/m^3, and 28.012 μg/m^3 were tested. Because the Tekran calibrator was designed to perform in lower ranges, the upper measurement ranges of the instruments could not be evaluated. Table 2-1 shows the associated flow rates and source temperatures for each challenge concentration.

Table 2-1. Tekran Source Temperatures and Flow Rates for Hg Challenge Concentrations

Generated Hg Vapor (µg/m^3)	Hg Source Temperature Set Point (°C)	Source Flow Rate (mL/min)
0.00	-	0
0.250	4.0	2.1
0.501	4.0	4.19
1.100	4.0	9.21
4.700	7.0	23.87
17.11	25.0	18.51
28.01	25.0	30.33

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was employed to make quantitative measurements of NH_3 in the bulk flow. FTIR is capable of measuring both inorganic and organic species in complex matrices due to the specificity of the wavelength for the corresponding analyte. FTIR relies on the specific vibrational energy (wavelength) transitions of IR light being absorbed by a molecule. Molecules sensitive in the IR region generate a specific spectral plot, with sharp peaks in various regions of the plot depending on the particular molecule or class of molecule. This molecular dependence allows FTIR to measure multiple species of both organic and inorganic compounds simultaneously.

Measurements for NH_3, the interference gas, were made using an FTIR system (MultiGas 2030 CEM, MKS Instruments Inc., Andover, MA). This system has a 5.11-meter path length cell, and the gas flow rate from the mercury generator and ammonia tank being analyzed was approximately 4 liters per minute (LPM). The system is designed to operate at 191°C for applications such as stack monitoring and combustion emissions monitoring. The high-temperature cell allows the system to measure water vapor up to 40% by volume and minimize acid gas condensation. The system's detector is liquid-nitrogen cooled and uses a helium neon reference laser. The data acquisition system collects and averages 64 scans over a one-minute period to generate an average NH_3 concentration. The data collection software generated a text spreadsheet file with the various component concentrations, operating data such as pressure and temperature, and spectra residuals or detection limits.

2.4 Portable Mercury Detectors

Five commercially available portable Hg detectors were evaluated in this investigation: the Lumex RA-915+, RA-915M, and Light 915 (Ohio Lumex, Cleveland, OH), and AMETEK's Jerome® J505 and Jerome® J405 (AMETEK Arizona Instruments, Chandler, AZ). Due to multiple malfunctions with the Lumex Light 915, testing was not able to be completed with this second-generation instrument. Testing is anticipated for the next generation of the Lumex Light (to be available in 2019to assess its capabilities for clearance sampling compared to the other detectors.

Detector testing requires a basis for establishing the performance of the tested technologies. For this evaluation, the assessment of technology performance was based on the delivery of known concentrations of Hg and interferents in controlled clean airstreams. NIST-traceable saturated mercury vapor generated by a Tekran® Model 3310 Elemental Mercury Calibrator was used to confirm the delivered concentrations and test conditions. It should be noted that this laboratory comparison is under controlled conditions and is not intended to simulate a mercury spill in a residential setting where additional interferences such as dust, dirt and other factors such as a recirculating heat or air conditioning system may affect monitoring. However, for an initial comparison to known concentrations of Hg vapor under specific test conditions, this was a necessary first step in evaluating the portable instruments.

2.4.1 Lumex Hg Detectors

The Lumex RA-915+ has been discontinued and replaced by the RA-915M, but the 915+ is still being serviced. It has historically been used for clearance sampling by EPA. As an updated version of the RA-915+, the RA-915M offers the same design and engineering as its predecessor but includes features such as a new lightweight outer casing, built-in backlit screen display, an automated calibration test cell, and a USB cable connection. All Lumex instruments use atomic absorption technology for detection as well as Zeeman Background Correction to eliminate interference. The detection range of the RA-915+ is 2.0 ng/m^3 to 20,000 ng/m^3 and for the RA-915M is 2.0 ng/m^3 to 30,000 ng/m^3 in ambient air. These instruments are typically used for the clearance of Hg-contaminated areas, and the 915+ has been identified as an acceptable alternative (ATSDR, 2012) to the modified NIOSH 6009 method (US EPA, 2012). These Lumex instruments are not necessarily appropriate for initial screening following a Hg spill indoors since the upper limit of detection is similar to or less than time-weighted average occupational exposure limits for Hg (25-50 μg/m^3). ATSDR considers readings from a properly calibrated Lumex Mercury Vapor Analyzer, that are representative of 8 hours of exposure at the point of sampling, as comparable to the NIOSH 6009 method in the range of 0.1-10 ug/m^3 (Singhvi, 2003) and will accept these in lieu of laboratory analysis (ATSDR. 2012). The Lumex Light-915 is a "scaled-down" version of the 915M and is appropriate for ambient air measurement applications that do not require the lower detection limits of the others. The detection range of the Light-915 is reported to be 0.10 μg/m^3 – 3,000 μg/m^3. Figure 2-2 shows the Lumex Hg detectors.

Figure 2-2. Lumex RA-915+, 915M, and Lumex Light-915 detector

2.4.2 Jerome Hg Detectors

The Jerome® J405 (Figure 2-3) is a portable Hg air monitor that has been redesigned in recent years to increase its sensitivity. The J405 utilizes the industry-proven, inherently stable, and reliable gold film sensor technology and simple, one-button operation. This sensor requires periodic sensor regeneration. The monitor has an ergonomically designed handle, a more lightweight exterior case, and significantly lower detection capabilities (0.5 μg/m^3). The J405 has a detection range of 0.5 μg/m^3 to 999 μg/m^3 with a resolution of 0.01 μg/m^3. It is equipped with an internal pump that draws the sample at a flow rate of 750 ± 50 mL/min as well as an optional internal data logging system.

The Jerome® J505 detector (Figure 2-3) is a portable fluorescence spectroscopy analyzer, which allows the detection cell to be simpler, smaller, lighter weight, and more durable than competing spectroscopy instruments. The highly efficient optical cell requires less flow to purge the system than other detectors, allowing the J505 to run at a lower flow rate, minimizing sample dilution. This feature eliminates nearly all interferences. The J505 has a detection range of 0.05 μg/m^3 to 500 μg/m^3 with a resolution of 0.01 μg/m3. It is equipped with an internal pump that draws the sample at a flow rate of 1 L/min as well as an optional internal data logging system.

Figure 2-3. Jerome J405 and J505 detectors

2.5 Measurement of Temperature and RH

The RH and temperature in the chamber were measured with a Vaisala HMP110. A K-type thermocouple was used for the primary temperature measurement. Both of the instruments were used to monitor the conditions in real time. The specifications for the Vaisala transmitter and the K-type thermocouple are shown in Table 2-2.

Table 2-2. Relative Humidity and Temperature Measurement Specifications

Parameter	Vaisala HMP110	K-Type Thermocouple
RH range (%)	0 – 100	NA
RH accuracy: 0–90%	±1.5%	NA
RH accuracy: 90–100%	±2.5%	NA
RH resolution	0.001%	NA
Temperature range	-14 to 80 °C	-200 to 1200 °C
Temperature accuracy	±0.2 °C @ 20 °C	± 1.2 °C @ 25 °C
Temperature resolution	0.001 °C	0.01 °C

3. Results

This section discusses the testing results for both the Lumex and AMETEK series of detectors at the selected Hg concentrations and under different operating conditions. The Ohio Lumex instruments (915+, 915M, and 915 Light) reported Hg concentrations in ng/m^3. Results from the other instruments reported in this section were converted to µg/m^3 for consistency. Additionally, standard curves, best-fit equations, and R^2 values are provided for the responses over the entire challenge concentration range (0 to 28 µg/m$^{3)}$ and up to 1.10 µg/m^3 Hg to assess the linearity at the lower concentration range.

3.1 Environmental Test Conditions

The target environmental conditions for accuracy and precision tests (Table 3-1) were intended to replicate real-word operating temperatures and RH conditions. Table 3-1 details the average temperature (ºC) and RH (%) of the bulk gas measured at the sampling manifold, and the room temperature of the test facility at each environmental condition.

Table 3-1. Average Environmental Conditions

Environmental Condition	Avg. Room Temperature (± RSD)	Avg. Manifold Temperature (± RSD)	Avg. Manifold RH (± RSD)
A	10.02 ± 0.078	9.9 ± 0.020	19.5 ± 0.26
B	23.8 ± 0.017	23.5 ± 0.0081	29.7 ± 0.029
C	34.9 ± 0.021	35.6 ± 0.0049	59.6 ± 0.037

RSD = Relative Standard Deviation

The results demonstrate that the environmental conditions were fully controlled and are within the acceptance criteria set for the data quality indicators (DQIs) listed in Table 3-2 for this project.

Table 3-2. DQIs for Critical Measurements

Measurement Parameter	Analysis Method	Accuracy Target
Real-time Hg concentration	Tekran Hg calibrator	±5%
RH (%)	Vaisala HMD53 (0-100%)	± 3.5% full scale from factory
Temperature (T)	K-type thermocouple	± 2 °C
Differential time	Computer clock	1% of reading

3.2 Cold Start Evaluation

The purpose of the rapid response tests was to determine the time required for readiness, accuracy, and speed after powering on the instrument following storage in a temperature-controlled environment ≈5 °C and 24 °C for replicating cold and hot startup temperatures, respectively. For comparison, these characteristics were evaluated first the J405, J505, and 915M instruments powered off and stored overnight at an ambient temperature and then when powered off and stored overnight in a laboratory refrigerator. The cold start testing evaluation was performed in a temperature-controlled laboratory environment.

The Lumex 915+ was not included in the rapid response/cold start testing due to an unidentified malfunction. When attempting to take samples with the unit, the display screen read “Low Rad” and the Hg concentration readings were very unstable. The Lumex 915+ was operable during every other test. Similarly, the 915-Light was not available for this rapid response/cold start evaluation at the time of testing due to an ongoing malfunction.

Prior to conducting the cold storage series of the rapid response tests, the detectors were stored overnight in the refrigerator for approximately 23.4 hours at an average temperature of 4.6 °C (± 0.30 RSD) and an average RH of 68.4 % (± 0.086 RSD). Prior to the ambient storage evaluations, the detectors were powered off and placed on a laboratory bench in the temperature-controlled laboratory.

The challenge gas was generated and brought to stable temperature and RH conditions prior to testing. Once the temperature and RH of the challenge gas were stable, a detector was removed from the refrigerator (for cold storage tests) or the laboratory bench (for ambient storage tests), then connected to the sampling manifold and immediately powered on. The time required for the detectors to become ready for sampling once powered on, or the ready-time, was recorded. Each detector was evaluated individually while the others remained powered off in the storage location until testing.

Table 3-2 details the ready-time for the detectors both immediately following storage at room temperature and after overnight cold storage.

Table 3-2. Measured Ready-Time Following Ambient and Cold Storage

Detectors Following Ambient Storage			
Start-up Step	**Time (hh:mm:ss)**		
Detectors	**J405**	**J505**	**915M**
Power On (time)	16:21:23	15:47:30	16:31:35
Ready to Sample (time)	16:21:25	15:50:12	16:31:42
Total Time (s)	2	162	7
Detectors Following Cold Storage			
Detectors	**J405**	**J505**	**915M**
Power On (time)	15:48:05	15:59:34	16:17:25
Ready to Sample (time)	15:48:08	16:05:47	16:17:30
Total Time (s)	3	373	5

The Jerome J405, which uses a gold film sensor technology, and to a lesser extent the Lumex 915M, which uses cold vapor atomic absorption spectroscopy, produced measured ready-time responses of 2 to 3 seconds and 5 to 7 seconds, respectively, independent of the temperature of the sensors. The Jerome J505, which uses the atomic fluorescence spectroscopy technique, produced measured ready-time responses on the order of minutes rather than the seconds reported for the other two tested detectors. The Jerome J505 ready-response time doubled when it was powered on following overnight cold storage at 4.6 °C compared to when it was stored in ambient temperatures overnight. The relatively higher ready-time for the J-505 is due to a prescribed warming and stabilizing sequence included in the control system of the instrument. Sampling can be triggered only when a flashing "Warming Up" message displayed on its screen disappears.

3.3 Detector Response Evaluation

Relative accuracy was the measure used for evaluating the acceptability of the tested detectors by comparison against concurrent set outputs of the Tekran calibration system used as the RM. At each environmental condition, the response of each detector was recorded approximately every 2 minutes over a 20-minute test duration. Precision, as assessed by the RSD, was represented by the reproducibility of the detector's response during the 20-minute exposure.

According to EPA PS 12A, an instrument is accurate if its measurements are with 20% RA relative to the standard method used. Alternatively, if the mean RM is less than 5.0 µg/dscm, the results are acceptable if the absolute value of the difference between the mean RM and the instrument values does not exceed 1.0 µg/dscm.

Table 3-3 lists the average response (µg/m^3 Hg), RPD (%), RA (%), and Precision (%) for each detector and at each prescribed condition.

Table 3-3. Average Detector Response and Accuracy per Environmental Conditions

Jerome Detectors

Environmental Conditions	Challenge Concentration (µg/m^3)	J405				J505			
		Avg. Hg Response (µg/m^3)	RPD (%)	Relative Accuracy (RA) [%]	Precision (%)	Avg. Hg Response (µg/m^3)	RPD (%)	Relative Accuracy (RA) [%]	Precision (%)
Condition A (10 ˚C, 19% RH)	0	NR		NA		0.017	NA	NA	
	0.25	NR		NA		0.26	4.00	23.9	17.3
	0.5	NR		NA		0.51	2.00	10.4	6.08
	1.1	0.576	-47.6	52.2	7.05	1.14	3.64	7.36	2.97
	4.7	5.09	8.30	10.2	1.34	4.93	4.89	6.12	0.99
	17.1	21.05	23.1	25.5	1.59	17.63	3.10	3.76	0.51
	28.01	35.49	26.7	28.2	0.93	28.44	1.54	2.10	0.45
Condition B (23 ˚C, 30% RH)	0	NR	NA			0	NA		
	0.25	NR	NA			0.25	0.00	19.8	14.6
	0.5	NR	NA			0.5	0.00	8.22	5.87
	1.1	0.1	-90.9	117	230	1.09	-0.91	5.38	3.91
	4.7	4.71	0.21	2.01	1.42	4.81	2.34	3.37	0.82
	17.1	20.27	18.5	20.8	1.53	17.29	1.11	1.49	0.32
	28.01	34.48	23.1	24.27	0.766	28.39	1.36	1.91	0.46
Condition C (35 ˚C, 60% RH)	0	NR	NA			0.1986	NA		
	0.25	0.496	98.4	235	55.3	0.178	-28.8	47.5	8.20
	0.5	0.804	60.8	144	41.7	0.429	-14.2	22.5	3.00
	1.1	1.52	38.2	66.7	16.8	0.952	-13.5	16.7	1.203
	4.7	5.17	10.0	22.8	9.45	4.229	-10.0	11.4	2.061
	17.1	17.70	3.51	6.22	1.92	14.75	-13.7	16.0	0.694
	28.01	31.80	13.5	14.8	0.952	24.77	-11.6	12.3	0.690

RA = within EPA acceptance criterion

NR = No response from detector; NA = Not applicable

Lumex Detectors

Challenge Concentration ($\mu g/m^3$)	Challenge Concentration ($\mu g/m^3$)	915M				915+			
		Avg. Hg Response ($\mu g/m^3$)	RPD (%)	Relative Accuracy (RA) [%]	Precision (%)	Avg. Hg Response ($\mu g/m^3$)	RPD (%)	Relative Accuracy (RA) [%]	Precision (%)
Condition A (10 ˚C, 19% RH)	0	0.0126	NA	NA		0.0054	NA	NA	
	0.25	0.225	-10.0	11.4	1.21	0.222	-11.2	12.0	0.653
	0.5	0.496	-0.80	1.82	0.878	0.497	-0.60	1.11	0.395
	1.1	1.125	2.27	2.45	0.135	1.158	5.27	5.46	0.122
	4.7	4.818	2.51	2.60	0.062	4.729	0.62	0.91	0.236
	17.1	17.64	3.16	3.62	0.370	17.93	4.85	5.54	0.526
	28.01	28.39	1.36	1.47	0.100	30.63	9.35	9.35	0.000
Condition B (23 ˚C, 30% RH)	0	0.0017	NA	NA		0.0031	NA	NA	
	0.25	0.208	-16.8	21.9	4.84	0.231	-7.60	42.9	30.80
	0.5	0.449	-10.2	10.5	0.215	0.449	-10.20	10.7	0.408
	1.1	1.016	-7.64	7.80	0.159	1.026	-6.73	7.12	0.321
	4.7	4.353	-7.38	7.62	0.205	4.238	-9.83	10.1	0.199
	17.1	15.91	-6.96	7.26	0.284	16.20	-5.26	5.26	0.000
	28.01	25.71	-8.21	8.36	0.136	27.05	-3.43	5.34	1.579
Condition C (35 ˚C, 60% RH)	0	0.0031	NA	NA		0.0059	NA	NA	
	0.25	0.178	-28.8	43.1	16.32	0.1202	-51.92	54.4	54.38
	0.5	0.375	-25.0	25.4	0.49	0.3163	-36.74	37.5	0.95
	1.1	0.851	-22.6	23.9	0.55	0.7275	-33.86	34.1	0.30
	4.7	3.776	-19.7	19.9	0.25	3.342	-28.89	29.1	0.24
	17.1	13.04	-23.7	26.7	3.11	12.44	-27.25	28.0	0.83
	28.01	21.94	-21.7	22.1	0.46	19.97	-28.70	29.6	0.94
RA = within EPA acceptance criterion					NR = No response from detector; NA = Not applicable				

The following section discusses the results listed in Table 3-3, summarizing the performance of each detector at different environmental conditions and Hg concentration levels.

3.3.1 Jerome 405

Condition A (10 ˚C, 19% RH)

The J405 failed to detect Hg concentrations ≤ 0.5 µg/m^3. The detector response rendered the highest RA when exposed to 4.7 µg/m^3, in compliance with the EPA PS 12A for acceptable performance. The RA significantly decreased when exposed to both lower and higher concentrations but, more so at lower concentrations.

At 1.10 µg/m^3, the precision (RSD) for the average response was 7.1%. The precision of the instrument improved and was relatively stable for target Hg measurements between 4.70 µg/m^3 and 28.01 µg/m^3, with an RSD between 0.93 and 1.6%.

Condition B (23 ˚C, 30% RH)

As with Condition A, no Hg measurements were observed at or below the challenge concentration of 0.5 µg/m^3. At the challenge concentration of 1.10 µg/m^3 the average detector response was 117% below the actual concentration. The RA improved significantly during the 4.7 µg/m^3 exposure, with an average response 2% above the actual concentration. A significant decrease in RA occurred when the challenge concentration increased to 17.1 µg/m^3 (20.8% RA) and then slightly decreased again at 28.01 µg/m^3 (24.3% RA). During the evaluation, the detector demonstrated optimal accuracy at the challenge concentration of 4.7 µg/m^3.

The calculated precision at the 1.1 µg/m^3 challenge concentration was very poor, with an RSD of 230%. The precision was found to increase as the challenge Hg concentrations were set at or above 4.7 µg/m^3. Within this elevated concentration range, the detector operated with optimal precision between 0.77 and 1.5% RSD.

Condition C (35 ˚C, 60% RH)

At this environmental condition, the level of accuracy of Hg detection was reduced from 1.1 µg/m3 to 0.25 µg/m^3. A significant increase in accuracy occurred as the challenge concentration increased from 1.10 µg/m^3 (66.7% RA) to 17. 1 µg/m^3 (6.22 RA%). The detector response was found to be in compliance with EPA PS 12A for concentrations above 17.1 µg/m^3.

The precision of the instrument was found to increase as the challenge concentration increased from 0.25 µg/m^3 (RSD = 55.3%) to 28.01 µg/m^3 (RSD = 0.95%).

3.3.2 Jerome 505

Condition A (10 ˚C, 19% RH)

The Jerome 505 detector was found to be more sensitive than the Jerome 405 and was able to detect Hg concentrations at 0.25 µg/m^3. The accuracy of the instrument was increased with increasing target Hg concentrations, with an RA of 23.9% at the 0.25 µg/m^3 to less than 10.4% for subsequent concentrations.

The precision was found also to increase from the lowest target Hg concentration (0.25 µg/m^3, RSD = 17.3%) to the highest target concentration (28.1 µg/m^3, RSD = 0.45%).

Condition B (23 ˚C, 30% RH)

There was no significant change in either the relative accuracy or in the precision of the detector with an increase in temperature and RH under condition A (10 ˚C, 19% RH).

Condition C (35 ˚C, 60 %RH)

The relative accuracy appeared to be impacted by an elevated RH and temperature conditions at the lower target Hg concentration of 0.25 µg/m^3 with an RA greater than 47%, and to a lesser extent at higher concentrations.

The precision of the average responses for the Hg challenge concentrations was found to be dependent on the target Hg concentration mimicking the results obtained with conditions A and B. The precision was relatively stable at concentrations ≥ 0.5 µg/m^3, which was ostensibly less susceptible to fluctuations in the input challenge concentrations. At these elevated T and RH conditions, the Jerome 505 tended to underestimate Hg concentrations, while at ambient and low T and RH conditions, this was not the case.

3.3.3 Lumex-RA-915M

Condition A (10 ˚C, 19% RH)

Overall, the RA of the Lumex-RA 915M was in compliance with EPA PS 12A (< 20% RA) for Hg measurements at all concentration levels tested in this study. The RA of the instrument increased with increased Hg concentrations from 11.4% RA at 0.25 µg/m^3 to less than 1.5% RA at 28.01 µg/m^3.

The precision of the 915M was very high for the range of Hg concentrations evaluated in this study, with less than 0.3 % RSD for Hg challenge concentrations greater than 0.5 µg/m^3.

Condition B (23 ˚C, 30% RH)

The RA of the instrument was found to decrease from 3.89 ± 3.75 % to 10.6 ± 5.67 % when the environmental conditions shifted from Condition A to Condition B. However, according to EPA PS 12A criteria, the instrument was accurate for target Hg concentrations greater than 0.5 µg/m^3 (RA ≤10.5%), and a precision less than 0.3%.

Condition C (35 ˚C, 60% RH)

Increasing both the temperature and the RH had a significant effect on the accuracy of the detector. Relatively few of the targeted Hg concentrations measured were within the acceptable EPA PS 12A criteria for an accurate continuous emission Hg instrument. Since the tested condition included both elevated temperature and RH, it could not be determined which variable effected the detector measurements.

3.3.4 Lumex-RA-915+

All Tested Conditions

No substantial differences in performance were observed for the Lumex-RA 915+ instrument when compared to the Lumex-RA 915M in terms of accuracy or precision, as shown in Table 3-3 for all of the target Hg concentrations tested.

3.4 Detector Linearity

One of the parameters that is used to assess the performance of an instrument is the linearity of its calibration curve. A calibration curve was determined for each detector to predict the unknown Hg concentrations based on the response of the instrument to the known standards (or set concentrations) of the Tekran calibrator using the least square method. Linearity of the calibration curve is usually expressed through the coefficient of determination, r^2. The slope of the calibration curve was used to determine the variance between the NIST-traceable Hg generator and the actual measured values of the detector.

The linear regression line for the Jerome J405 detector, for relatively low temperature and RH environmental conditions (Conditions A and B), is shown in Figure 3-1. The Jerome J405 exhibited a slope of 1.22, tending to overestimate the Hg concentration. The linearity of this instrument appears to be good (R^2 >0.99) for concentrations greater than 1.1 $\mu g/m^3$, with a systematic bias of greater than 22%. The LOD was not calculated for this instrument since no response was detected for Hg concentrations lower than 1.1 $\mu g/m^3$, and no measurements were made between 5.0 and 1.1 $\mu g/m^3$.

The Jerome J505, as shown in Figure 3-2), exhibited a slope near a value of 1 (>0.97) with relatively a good linearity (R^2 >0.99) for Hg concentrations between 0 and 28.01 $\mu g/m^3$. The average calculated LOD based on linear regression for this instrument was 0.07 $\mu g/m^3$.

Both Lumex detectors (915M, and 915+), shown in Figures 3-3, and 3-4, exhibited similar slopes (0.91 and 0.93), respectively. They tend to slightly underestimate the value of the Hg concentration of the Tekran calibrator (Figures 3-3, and 3-4). The linearity of the two detectors (R^2 = 0.98 and 0.96, respectively), and the calculated LODs (<0.002 $\mu g/m^3$) were also found to be similar and within an acceptable range.

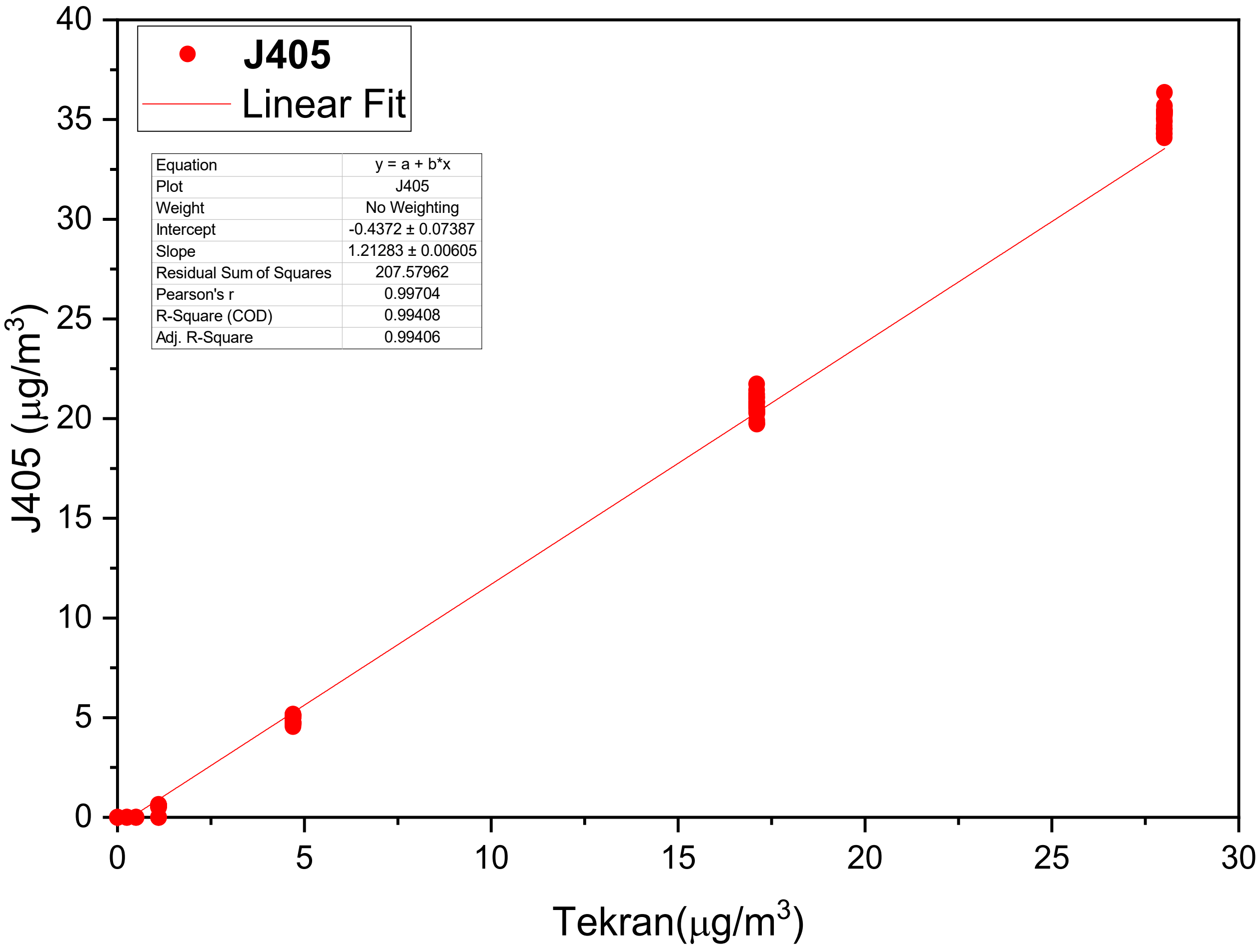
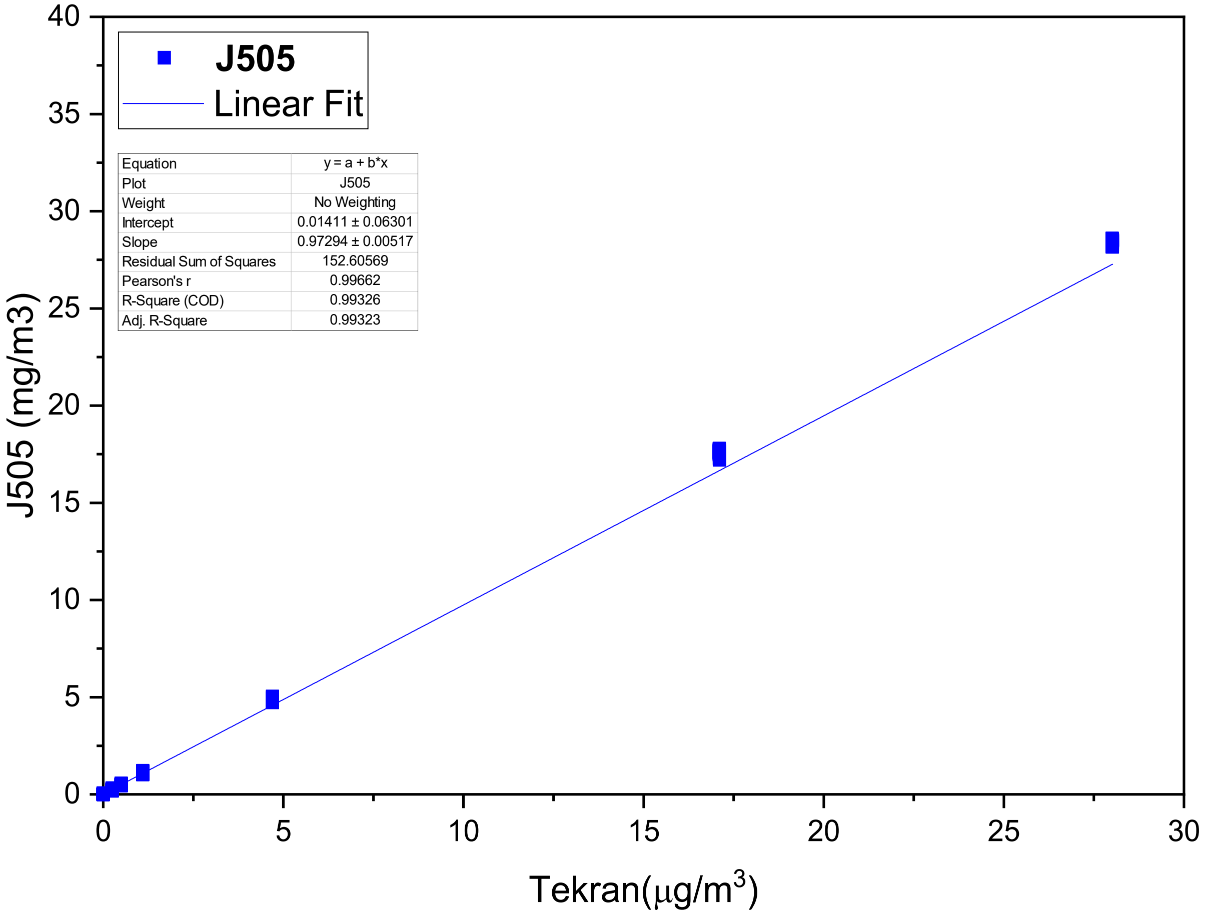


Figure 3-1. Jerome J405 Linear Regression Curve



Equation	y = a + b*x
Plot	J505
Weight	No Weighting
Intercept	0.01411 ± 0.06301
Slope	0.97294 ± 0.00517
Residual Sum of Squares	152.60569
Pearson's r	0.99662
R-Square (COD)	0.99326
Adj. R-Square	0.99323

Figure 3-2. Jerome J505 Linear Regression Curve

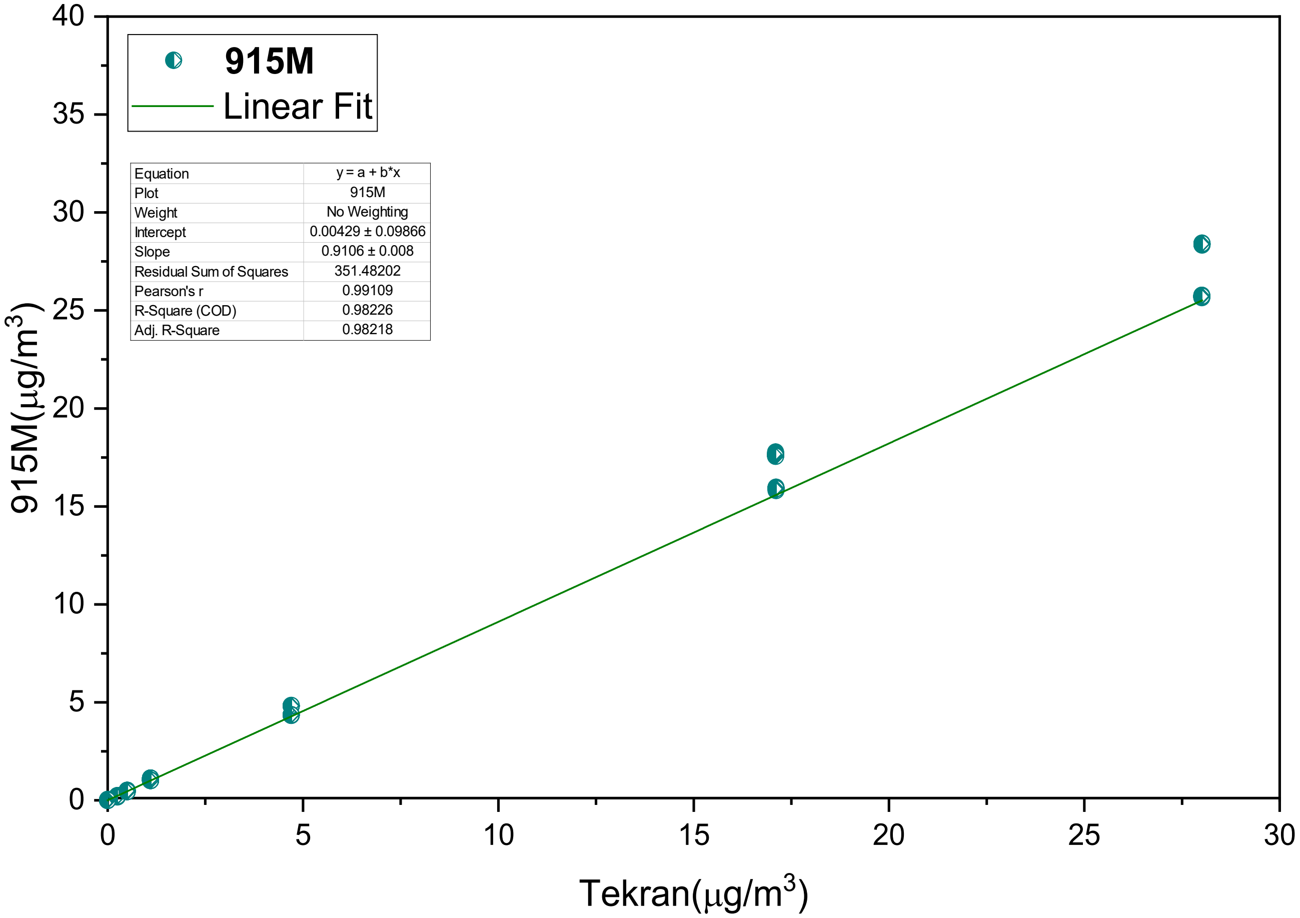


Figure 3-3. Lumex 915M Linear Regression Curve

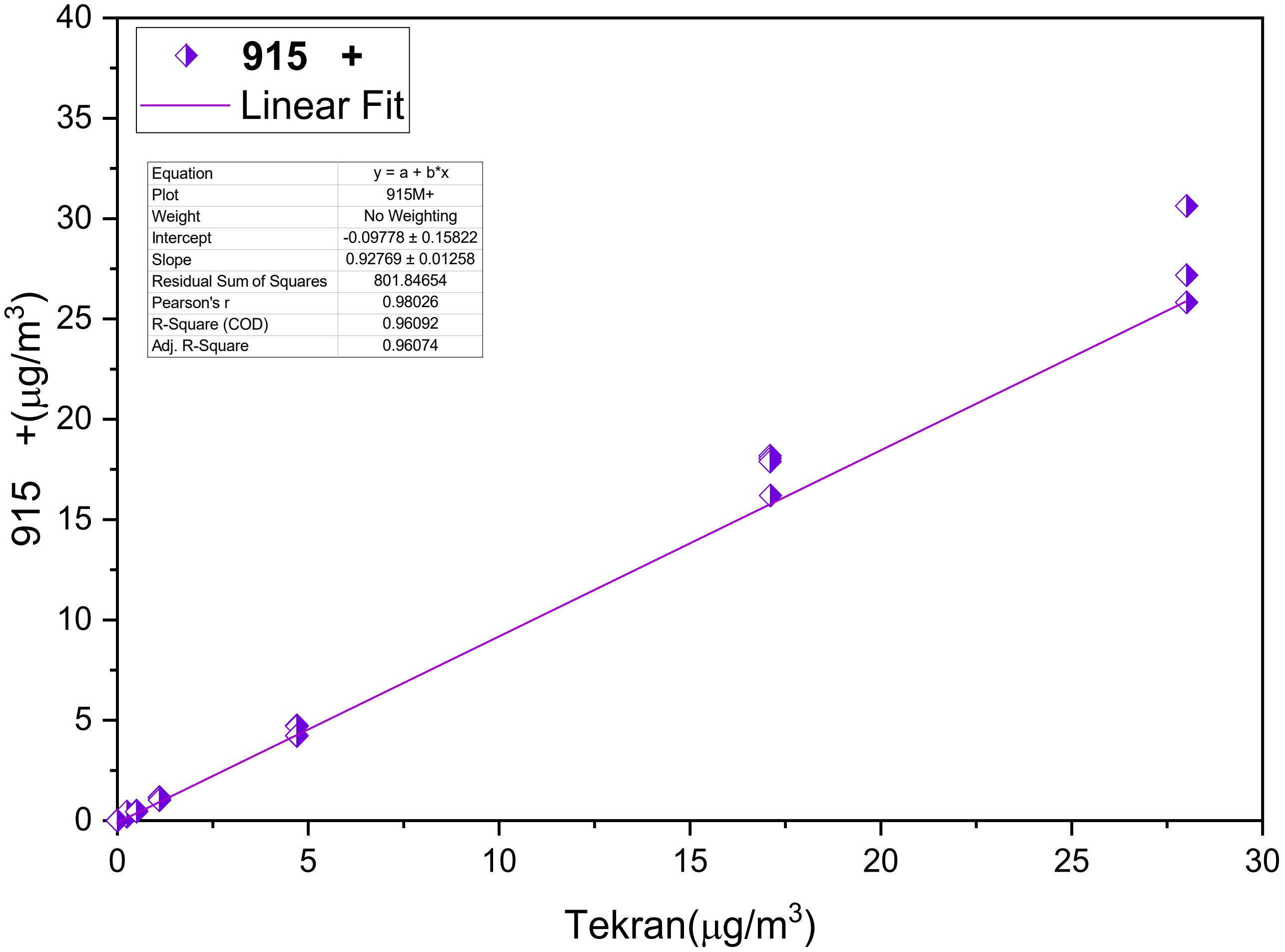


Figure 3-4. Lumex 915+ Linear Regression Curve

3.5 Interference Evaluation

Interference testing was performed by introducing a gas mixture containing NH_3 (7.863 ppm sulfur hexafluoride, 514.9 ppm ammonia, and balance nitrogen) downstream of the Tekran and RH equipment. The target NH_3 concentration was the odor threshold of 8 to 10 ppm.

The interference evaluation was initially designed to include the J405, J505, RA-915M, RA-915+, and the RA-915 Light detectors. Within 2 weeks prior to testing, the 915 Light detector underwent calibration by the manufacturer. However, three days into the interference evaluation, the detector experienced an undiagnosed malfunction despite being re-evaluated by the manufacturer a second time. Due to the repeated malfunctions of this instrument, the interference evaluation for this detector is not reported.

The target environmental conditions for interference evaluations were 23 °C and 30% RH. Table 3-4 details the actual temperature and RH measurements for both of these tests.

Table 3-4. Average Environmental Conditions

Environmental Conditions	
Avg. Room Temperature (°C ± SD)	23.0 ± 0.11
Avg. Manifold Temperature (°C ± SD)	23.0 ± 0.08
Avg. Manifold RH (% ± SD)	30.0 ± 0.58

Baseline comparisons were performed at select concentrations to evaluate response with the detector exposed to Hg gas both with and without NH_3 interference at constant RH and constant temperatures and a minimal time difference between the interferent levels (present and not present).

To minimize the potential for changes in the system, comparisons for each Hg level were performed in succession, first with the interferent gas and then without it. Hg measurements were collected after a 20-minute transition from the shutoff or opening of the NH_3 feed downstream of the Tekran calibrator output feed to allow the detectors and the FTIR to stabilize. The selected Hg challenge concentrations with and without NH_3 were 0.0 µg/m^3 and 4.70 µg/m^3, respectively.

The actual average concentrations of NH_3 and method detection limits (MDLs) are presented in Table 3-5. The MDLs were generated by multiplying the value of the spectral residuals generated by the software by three.

Table 3-5. Average NH_3 concentration (ppm ± SD)

Hg Setpoint (µg/m^3)	NH_3 (ppm)	
	Average	MDL
0.0	7.79 ± 0.08	0.07
4.70	8.13 ± 0.29	0.081

The results of the interference testing (average response [µg/m^3 Hg]), precision [%], and RA) for each detector, with and without the NH_3 interferent, are presented in Table 3-6.

Table 3-6. Average Detector Response and Accuracy per Environmental Conditions With and Without NH_3 Interferent

Jerome Detectors							
Challenge Concentration (µg/m3)	NH_3 (Interferent)	J405			J505		
		Avg. Hg Response (µg/m3)	Relative Accuracy (RA) [%]	Precision (%)	Avg. Hg Response (µg/m3)	Relative Accuracy (RA) [%]	Precision (%)
0	No	NR	NA		0.042	NA	
	Yes	NR			0.036		
4.7	No	5.09	18.2	7.43	4.81	3.37	0.82
	Yes	5.34	29	10.8	4.9	5.71	1.09

Lumex Detectors							
Challenge Concentration (µg/m3)	NH_3 (Interferent)	915M			915+		
		Avg. Hg Response (µg/m3)	Relative Accuracy (RA) [%]	Precision (%)	Avg. Hg Response (µg/m3)	Relative Accuracy (RA) [%]	Precision (%)
0	No	0.047	NA		0.025	NA	
	Yes	0.031			0.016		
4.7	No	4.41	6.1	0.03	4.259	9.5	0.13
	Yes	4.38	7.8	0.76	4.238	11.1	1.14

3.6 Operational Observations

Operational observations for each of the detectors are presented in Table 3-7.

Table 3-7. Operational Considerations for use of the Hg Detectors

Hg Detector	Operational Observations
Jerome J505/J405	Option to save and transfer test data to a USB. Additionally, the tests could be conducted by manually starting the analysis (pushing the "Test" button) or the unit could be programmed to test at specific time intervals. The latter option works well with the USB data retrieval.
Lumex RA 915M	The option to connect the unit to a computer with a data cord was available but not utilized.
Lumex RA 915+	There was not an option to save data for future retrieval or transport data to a portable storage device. Data had to be recorded manually. The lamp could be lit manually if necessary. Specific computer software was not required.
Lumex RA 915 Light	The free manufacturer-provided software allowed, with a computer and data cord connection, remote observation of real-time test data. Additionally, system diagnostics and actions such as turning the pump on and off and lighting the lamp can be performed with the software. There is no option to relight the lamp manually.

3.7 Summary of Detector Performance

Five commercially available portable Hg detectors from two vendors (AMETEK Arizona Instruments and Ohio Lumex) were evaluated for their performance against NIST-traceable saturated mercury vapor generated by a Tekran® Model 3310 Elemental Mercury Calibrator. The five Hg instruments evaluated were AMETEK's Jerome® J405, and Jerome® J505, and Lumex's RA-915+, RA-915M, and Lumex Light 915.

The calibrated instruments were on loan by the manufacturers and used as received. The setup and operation of all the tested detectors was relatively simple, with no further calibration or on-site modification required. Due to multiple malfunctions with the Lumex Light 915, testing was completed with this second-generation instrument. In terms of operability and data retrieval, the Jerome units and the Lumex RA 915M all include a USB interface for saving and transferring test data test data. The Lumex RA 915+ does not have an option to save data for future retrieval or transport data to a portable storage device.

The Jerome® J405 did not perform very well, with no detector responses for target Hg concentrations below 1.10 µg/m^3, and tended to overestimate the Hg concentration, with a systematic bias greater than 22%. The Jerome® J505, however, outperformed the Jerome J405 across the tested range of concentrations in terms of sensitivity, with an observed detector response at 0.25 µg/m^3. Moreover, the J505 was found to be compliant with EPA PS 12A and can be considered an accurate instrument for Hg target ranges between 0.25 to 28.0 µg/m^3, whereas the Jerome ® J405 did not demonstrate this accuracy.

Both Lumex-RA 915 M and Lumex-RA 915+ detectors were found to comply with the EPA PS 12A criteria for Hg measurements and rendered similar responses for the tested environmental conditions (10 ˚C, 19% RH, and 23 ˚C, 30% RH). Increasing both the temperature and the RH of the environmental conditions (35 ˚C, 60% RH) hindered the performance of both instruments; therefore, they cannot be considered accurate and reliable for high temperature and RH conditions according to the EPA's specifications.

The overall results indicate that none of the detectors' responses were affected by the presence of the NH_3 interferent at the target challenge concentrations (0.0 µg/m^3 and 4.70 µg/m^3). The accuracy and precision of the instruments were in general lower in the presence of NH_3, but not sufficiently significant to affect the performance of the instruments.

The setup and operation of all the tested detectors was relatively simple, with no calibration of the instruments required prior to their evaluation. The instruments were loaners from the manufacturers and used in the condition received. In terms of operability and data retrieval, the Jerome units, and the Lumex RA 915M included a USB interface for saving and transferring test data. The Lumex RA 915+ does not have an option to save data for future retrieval or transport data to a portable storage device.

Despite the successful testing of multiple ambient Hg monitors under varied conditions, there are still additional questions to be answered. Testing summarized in this report generally met project objectives to determine which instruments meet detection and sensitivity requirements, under controlled conditions, for assisting with a Hg clearance determination. However, providing additional data to strengthen support for these conclusions is warranted, including actual field test conditions. Further evaluation of these instruments could be performed over a larger Hg concentration range and under separate environmental conditions in addition to other improvements. Also, additional testing will include direct comparisons to the NIOSH Method 6009 laboratory-based sampling and include specific criteria as outlined in the EPA Emergency Response Team (ERT) SOP (US EPA/ERTC, 2004) for comparison in a representative "field" environment. Future recommended tests include:

- Extending the sampling time to 8 hours with the Lumex/Jerome J505 detectors and compare the results to the currently used modified NIOSH 6009 (sorbent tube).
- Extending the Hg concentration range to the upper capacities of the Jerome instruments
- Operating in separate high RH and high temperature environments to decouple their respective effect
- Adding additional interferents (e.g., volatile organic carbons) to the gas-containing Hg stream

- Testing of a third-generation Lumex Light against the Lumex 915M and other “good performing” detectors
- Testing multiple detectors (two or three) of the same type to investigate variation between instruments.

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