

APPENDIX A

Summary of Significant Mercury Responses

APPENDIX B

ATSDR Suggested Action Levels for Indoor Mercury Vapors
in Homes or Businesses with Indoor Gas Regulators

Suggested Action Levels for Indoor Mercury Vapors in Homes or Businesses with Indoor Gas Regulators

Purpose: This document is intended solely as a quick reference guide for use by public health and environmental officials in evaluating data collected from structures in which mercury pressure regulating devices for natural gas meters were moved from inside to outside the structures as part of a modernization process. It does not provide detailed justifications for environmental sampling requirements, as health consultations or environmental sampling plans may do.

In the past, ATSDR has been reluctant to provide a list of suggested action levels such as this because of the site specific nature of exposures. ATSDR has recognized that action levels can differ according to differing populations, exposure durations, concentrations, and specific hazards. However, the immediacy and extent of the potential health risk associated with mercury contamination in the present situation require publication of this guide. Many parts of the country may be affected by the possible exposure to mercury resulting from re-positioning of mercury-containing gas pressure regulators and the subsequent response efforts of gas utilities, public health and environmental officials. Moreover, the involvement of multiple health and environmental jurisdictions creates a need for consistency in presenting health risk information. Therefore, ATSDR, at the request of a state health department and an U.S. EPA regional office, is attempting to provide suggested action levels for various response activities under different exposure scenarios.

Background: In this context, an *action level* is an indoor air concentration of mercury vapor, which should prompt consideration of the need to implement a recommended response by public health and environmental officials. The various suggested action levels provided in this document are intended as recommendations, not as regulatory values or cleanup values, although some may correspond to present or future values adopted by regulatory authorities.

The suggested action levels presented in this document recognize that an individual must be exposed to a sufficient concentration over some specific period of time in order for mercury vapor to cause adverse health effects. The suggested action levels also recognize that while individual susceptibility may vary, developing fetuses and young children under six years old are generally at higher risk than others of incurring adverse health effects from exposure to mercury vapor. If the indoor air concentration corresponding to any suggested action level is exceeded, then a potential health risk may be present, and responders should evaluate the exposures at that location and consider implementing appropriate protective measures to reduce or eliminate the risk.

The suggested action levels presented here are based on data available in ATSDR's Toxicological Profile for Mercury (1999) or in the Hazardous Substance Databank of the Toxicology Data Network at the National Library of Medicine. ATSDR has also made use of additional data collected by the US Environmental Protection Agency (EPA) and of specific experiences of ATSDR at other sites. Other factors considered in the development include available information on normal background levels and analytical detection limits of various techniques for evaluating airborne contamination. Any information specific to the exposures at any given location as described below should also be considered before implementing a response action.

These suggested action levels are extrapolated from health guidance values (HGVs) independently developed by two federal agencies, ATSDR and EPA. These HGVs are based on both animal studies and human epidemiology studies that detail the health effects of inhalation of mercury-contaminated air. ATSDR has developed a chronic Minimal Risk Level (MRL) of 0.2 ug/m^3 that is based on a 1983 study of workers exposed to an average Lowest Observed Adverse Effect Level (LOAEL) of 26 ug/m^3 over an average of 15 years. This workplace average exposure was adjusted from a 40 hour per week exposure to a 168 hour per week exposure (i.e., 24 hours/day, 7 days/week) and then divided by an uncertainty factor of 30 to account for the use of the LOAEL and the different sensitivities of individuals. In addition, EPA has used the same study to develop a Reference Concentration (RfC) of 0.3 ug/m^3 , using different assumptions and uncertainty factors. ATSDR considers the RfC and the Chronic MRL to be the same value for all practical purposes. An MRL, then, is defined as an estimate of the daily exposure level to a hazardous substance (in this case, metallic mercury) that is likely to be without appreciable risk of adverse, non-cancer health effects (metallic mercury is not

considered to be a carcinogenic substance) over a specific exposure route and duration of exposure. For further information, see Section 2.5, Chapter 7, and Appendix A of the ATSDR Tox Profile and the EPA's Integrated Risk Information System (IRIS) on the Internet at www.epa.gov/ngispgm3/iris/index.html.

The suggested action levels in the tables below were designed for a group of structures where pressure regulators using approximately 2 teaspoons (and perhaps more) of mercury (~10 ml or 135 g) and the accompanying gas meters were re-positioned from the interior of buildings (including homes) to the exterior. During this adjustment of regulator location that may have taken place some time ago, mercury was spilled in some instances. However, spills of mercury may not have occurred indoors. Therefore, the categories of exposure include (a) buildings that may have had no spills; (b) buildings that had spills and needed cleanup but had air mercury levels that constitute no immediate health risk; and (c) buildings that had spills resulting in indoor air concentrations sufficient to warrant isolating humans from the exposure. In general, the screening for these homes or businesses consists of: (1) confirming that a natural gas meter had been in the building and moved outside; (2) observing the area where the gas meter had been originally for metallic mercury; (3) asking the resident if they had ever noticed metallic mercury in the vicinity of the gas meter; and, (4) evaluating the area with a Jerome™ meter or the equivalent. If there is any positive indicator of mercury on the Jerome Mercury Vapor Analyzer (a real-time air monitoring instrument) that cannot be explained by interferences, then the building is placed on the list for further characterization.

Visible mercury is not only a source of vapors but also a tracking hazard and an attractive nuisance. No matter what the airborne concentration is, free liquid mercury may pose a problem in the general population. Generally, a condition that no visible mercury be present is stipulated only at stages when cleanup is completed. This condition may be considered as much a check on the data quality as anything else. It is rare that liquid mercury exists at concentrations as low as would be considered safe in most exposure scenarios other than a workplace where mercury is used in the production process.

General Exposure Assessment Considerations: The primary route of entry for metallic mercury is by inhalation; ingestion and skin absorption of this form of mercury is usually not biologically significant. Sensitive populations to mercury exposure are those with developing central nervous systems, including young children and the fetuses of women who are pregnant. Other individuals of potential concern are those with pre-existing kidney conditions, usually at exposures to much higher concentrations than the first group. The specific exposure of these groups in any given situation should be considered when assessing the need for any given response action. Specific concerns are mentioned in the tables below. If there is any doubt, responders should consult with state or local public health officials before deciding on a course of action. Responders may also contact ATSDR at 404-639-0615, 24 hours a day.

Exposure Assumptions for Different Settings: For the purposes of this document, the residentially exposed population includes infants, small children, and pregnant women presumed to have inhaled mercury for a period up to 24 hours per day, 7 days per week potentially for months or even years. Occupational or commercial settings include those individuals that are primarily healthy adults exposed up to 8-10 hours per day, 40 hours per week, with transient exposures by sensitive populations (e.g., a retail establishment or schools). The concentrations provided as suggested action levels are for comparison to the environmental data collected in affected residences and workplaces.

Suggested Action Levels for Mercury (CAS # 7439-97-6) – Residential Settings [†]

Indoor Air Concentration (ug/m³)	Use of the Action Level	Rationale for Action Level	Method of Analysis *	Reference
≤1.0	Level acceptable for occupancy of any structure after a spill (also called the residential occupancy level.)	A spill occurred in this building, and the risk manager needs to know if the building is safe for occupancy. ATSDR would prefer no one ever be chronically exposed to concentrations above the MRLs; however, experience has shown cleanup operations in a response to concentrations below 1 ug/m ³ can be extremely disruptive to individual and family quality of life. While this concentration is slightly above HGVs, this level is still 25 times lower than the human LOAEL on which the MRL is based. An indoor air concentration of 1 ug/m ³ , as measured by the highest quality data (e.g., NIOSH 6009 or equivalent), is considered safe and acceptable by ATSDR, provided no visible metallic mercury is present.	NIOSH 6009 or equivalent	Based on HGVs above. ATSDR, 1999. EPA/IRIS
No qualitative detection on an Arizona Instrument's Jerome™ Meter.	Screening level for homes that had indoor gas meters with no evidence of a spill	Mercury was present in the regulator inside the home, but no evidence of a spill is found. The qualitative detection limit of the most commonly available air monitoring instruments approximates 1 order of magnitude below levels of known human health effects. As there was no spill, no visible metallic mercury should be present. Natural ventilation (e.g., windows, HVAC air changes, etc.) should reduce any concentration even lower with no disruption of family life or costs.	Real-time Air monitoring instrument (i.e., Jerome™ meter or equivalent)	
10	Isolate residents from the exposure	When adjusted from an intermediate to chronic exposures to a continuous exposure scenario (i.e., 24 hrs/day, 7days/week), this concentration approaches levels reported in the literature to cause subtle human health effects. Applied to acute exposures with good accuracy by real-time instruments, this value allows for interventions before health effects would be expected. Whenever possible, the mercury vapors should be prevented from reaching living spaces rather than temporarily relocating individuals. See the building evaluation protocol developed for these situations in your area and Section 2.1 of ATSDR's Toxicological Profile.	Real-time Air monitoring instrument (i.e., Jerome™ meter or equivalent)	ATSDR, 1999.
10	Acceptable level in a modified test procedure to allow personal effects to remain in the owner's possession	For personal effects, such as clothing, warmed in a discrete plastic container much smaller than a typical room (e.g., a garbage bag), this concentration in the air trapped inside the container is considered safe by ATSDR based on a number of factors.	Real-time Air monitoring instrument (i.e., Jerome™ meter or equivalent)	

* - Environmental analysis should be in accordance with the requirements specified by environmental authorities. When real-time air monitoring instruments are specified in this table, laboratory analysis may be substituted at the discretion of the risk managers involved in the event. Operation of real-time instruments should be in accordance with manufacturer's instructions.

[†] - Structures where mercury pressure regulating devices for natural gas meters were moved from inside the structure to outside the structure.

Suggested Action Levels for Mercury (CAS # 7439-97-6) – Occupational and Commercial Settings [†]

Indoor Air Concentration (ug/m³)	Use of the Action Level	Rationale for Action Level	Method of Analysis *	Reference
3.0	Re-occupancy after a spill of an occupational or commercial setting where mercury is not usually handled.	Based on residential occupancy level but adjusted for the shorter duration exposures typical of most workplaces. This concentration approximates one order of magnitude below levels of known human health effects, provided no visible metallic mercury is present to act as an attractive nuisance or a source for more vapors. Those exposed in this instance would not expect hazards associated with mercury as part of their normal work and may include transient exposures by more sensitive individuals (e.g., retail facilities).	NIOSH 6009 or equivalent	HGVs. ATSDR, 1999. EPA/IRIS
25	Occupational settings where mercury is handled. •	Based on the 1996 ACGIH TLV. Assumes hazards communications programs as required by OSHA; engineering controls as recommended by NIOSH; and medical monitoring programs as recommended by the ILO, NIOSH, and ACGIH are in place. This concentration is ½ the peer-reviewed 1973 NIOSH REL and 1/4 the regulatory 1972 OSHA PEL. See HSDB at toxnet.nlm.nih.gov/sis on the Internet.	Real-time Air monitoring instrument (i.e., Jerome™ meter or equivalent)	HSDB, 1999
25	Response Worker Protective Equipment Upgrade. •	Response workers subject to HAZWOPER should evaluate need to upgrade protective equipment. Based on the 1996 ACGIH TLV. Assumes hazards communications programs as required by OSHA; engineering controls as recommended by NIOSH; and medical monitoring programs as recommended by the ILO, NIOSH, AND ACGIH are in place. This concentration is half the peer-reviewed NIOSH REL and a quarter of the regulatory OSHA PEL. See HSDB at toxnet.nlm.nih.gov/sis on the Internet. For these workers, engineering controls are not typically in place, and it is not possible to control the exposure by other safety techniques.	Real-time Air monitoring instrument (i.e., Jerome™ meter or equivalent)	29 CFR 1910.120; 40 CFR 311; NIOSH, 1987
10,000	IDLH. Response Workers Protective Equipment upgrade.	Response workers subject to HAZWOPER should upgrade protective equipment. See http://www.cdc.gov/niosh/idlh/ on the Internet.	Real-time Air monitoring instrument (i.e., Jerome™ meter or equivalent)	29 CFR 1910.120; 40 CFR 311; NIOSH 1987

* - Environmental analysis should be in accordance with the requirements specified by environmental authorities. When real-time air monitoring instruments are specified in this table, laboratory analysis may be substituted at the discretion of the risk managers involved in the event. Operation of real-time instruments should be in accordance with manufacturer's instructions.

[†] - Structures where mercury pressure regulating devices for natural gas meters were moved from inside the structure to outside the structure.

• - Women workers in these settings who are pregnant or attempting to become pregnant should consult their physicians regarding their mercury exposure.

APPENDIX C

Comparison of Real-Time and Laboratory Analysis of Mercury Vapor

Comparison of Real-Time and Laboratory Analysis of Mercury Vapor in Indoor Air: Statistical Analysis Results

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Abstract

Metallic mercury vapor levels in indoor air were measured under various conditions inside a van and a trailer using Lumex RA915⁺ (Lumex) and Mercury Tracker 3000 (Tracker) real-time mercury analyzers and were confirmed by laboratory analysis using a modified National Institute for Occupational Safety and Health (NIOSH) 6009 method. Mercury monitoring data from several mercury spill sites around the United States were also used in this comparison study. Based on statistical analysis, Lumex and Tracker field analyzers provide real-time screening to assess initial extent of metallic mercury contamination, to identify "hot spots", and to monitor progress of decontamination procedures at a spill site.

Statistical analysis showed that field and laboratory (NIOSH 6009) data for analyses of mercury in air samples were comparable for Lumex and Tracker Hg readings of about 0.03 and 0.1 $\mu\text{g}/\text{m}^3$ or greater, respectively, provided that the factory calibrations of the real-time analyzers were adjusted based on the mercury concentration measured from a standard mercury gas source in a laboratory environment. In order to meet final clean-up action levels (0.3-1.0 $\mu\text{g}/\text{m}^3$) for indoor mercury spills, time averaged Lumex and Tracker results may be used instead of the NIOSH method under certain circumstances, such as during emergency responses, depending on site requirements. Additional work is in progress to define the conditions when real-time metallic mercury vapor monitoring instruments, such as the Lumex or Tracker, may be used.

1 Introduction

The quality of indoor air and the resultant risk associated with accidental exposure to volatilized metallic mercury (Hg) is a major concern for building occupants. Indoor air monitoring programs that can provide high quality data with rapid turnaround of results are needed to effectively address these concerns. The field and laboratory analytical methods developed by the United States Environmental Protection Agency's Environmental Response Team (U.S. EPA/ERT), through its Response Engineering Analytical Contract (REAC), provide timely, cost-effective elemental Hg analysis while maintaining rigorous Quality Assurance/Quality Control (QA/QC) procedures to ensure reliability of the analytical data. Use of field analyzers provides real-time screening to assess the initial

extent of metallic mercury contamination, to identify "hot spots", and to monitor progress of decontamination procedures at the spill site. For readings below field detection levels, the modified NIOSH 6009 method provides an effective way to measure low Hg vapor levels (Singhvi et al., 1999).

2 Analysis Methodology

Real-time mercury vapor measurements were logged to data files at regular intervals (typically 2 to 15 seconds) while indoor air samples were collected for laboratory (NIOSH 6009) analysis. The Lumex was operated in software "MONITORING" mode during data logging using an external computer. The Tracker has built-in data logging capabilities and the data were downloaded after collection using an external computer. The real-time mercury analysis results were then averaged over the appropriate period (typically 2-, 4-, or 8-hours) that coincided with the indoor air sample collection time. All comparisons are based on time averaged data.

2.1 Real Time Monitoring

Lumex RA915⁺: The Lumex is a portable atomic absorption spectrometer designed to detect extremely low mercury vapor concentrations and perform fast and simple analyses both at a fixed laboratory and in the field. Two modes of operation are available for ambient air analysis: "ON STREAM" and "MONITORING". At a sample rate of 10-15 liters per minute (L/min), the Lumex can detect mercury vapor in ambient air at concentrations as low as two nano grams per cubic meter (ng/m^3). The low mercury detection limit and the sensitivity of the instrument are achieved through a combination of 10-meter multi-path optical cells and Zeeman Atomic Absorption Spectrometry using High Frequency Modulation of polarized light. The Lumex is factory calibrated (from 1000 to 40,000 ng/m^3) and mercury vapor results are reported in ng/m^3 (Ohio Lumex Co., 2000).

Mercury Tracker 3000: The Tracker is a portable instrument based on resonance absorption of mercury atoms at a wavelength of 253.7 nanometers (nm). The mercury sample is drawn through a 1 micron PTFE filter, at approximately 1.2 L/min, into the optical cell of the instrument by a membrane pump. Radiation from a mercury lamp passes through the cell and is measured by a solid state ultraviolet (UV) detector. The attenuation of the UV light reaching the detector depends on the number of mercury atoms in the optical cell. The internal computer performs the quantitative evaluation of the mercury concentration in the sample in real-time. The Tracker is factory calibrated (from 60 to 300 $\mu\text{g}/\text{m}^3$) and mercury vapor concentration is reported in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) (Mercury Instruments Analytical Technologies, 2000).

2.2 Laboratory Analysis (NIOSH 6009)

Indoor air Sampling: Indoor air samples of volatilized elemental Hg are collected on solid sorbent material (typically HopcaliteTM or HydrarTM) contained in glass tubes. Air is pumped through the sorbent with a personal sampling pump, which can be programmed for collection time and flow rate [typically 0.25 to 0.75 L/min]. Pump flow rate is initially calibrated against a rotometer reference and is measured again after sample collection. Sampling stations are typically set up in several locations within the structure.

Modified NIOSH 6009 Method: The sorbent material from the collection tube (typically 200 milligrams in a single section) is quantitatively transferred to a 100-milliliter (mL) volumetric flask. The sample is digested by first adding 2.5 mL of concentrated nitric acid followed by 2.5 mL of concentrated hydrochloric acid. After digestion, the sample is diluted to volume with deionized water and analyzed using the cold-vapor Atomic Absorption spectroscopy technique. Results are reported as $\mu\text{g}/\text{m}^3$ based on the total air volume collected for the sample. Matrix effects are minimized by using sorbent material for preparation of blanks and calibration standards (U.S. EPA/ERTC, 2001). The modified NIOSH 6009 method incorporates more concentrated sample solutions than those of the standard method. This minimizes dilution effects while providing improved Hg detectability to meet the demanding action level requirements associated with emergency response situations.

3 Statistical Methods

Several statistical analysis methods may be used for evaluating and comparing field and laboratory data (Gilbert, 1987 and Draper and Smith, 1981). A probability-value (p-value) is usually included in the output. Irrespective of the analysis being performed, the p-value is the lowest level at which the proposed hypothesis can be rejected. If the p-value is less than the given significance level (usually 0.05), the hypothesis can be rejected, otherwise, there is no statistical significance and the hypothesis cannot be rejected. Prior to performing any statistical evaluations, a test of distribution is performed on the data set to determine if parametric or non-parametric statistical methods should be utilized.

3.1 Pairwise Comparisons

Pairwise comparisons are useful for initial evaluation of field versus laboratory data sets. This is a hypothesis test, run at a significance level of 0.05, which determines if there are significant differences between two sets of paired data. During the test, one data set is subtracted from the other to get a third set of differences. A statistical analysis is performed to test the null hypothesis that the mean of the differences equals zero. If the data are not normally distributed, a test about the median as opposed to the mean is performed. In both cases, the p-value determines the significance of the analysis. If the p-value is less than the significance level, the null hypothesis is rejected and there is significant difference between the data sets. If the p-value is greater than the significance level, there is no significant difference between the data sets. This does not mean that the data sets are equal, but, rather, that they are not significantly different from each other. Even if pairwise comparisons analysis indicates that field and laboratory data sets are significantly different, it does not mean that a strong relationship cannot exist between them.

3.2 Correlation Analysis

Correlation analysis is related to regression analysis. It determines the degree of linearity between two sets of data and may be utilized prior to linear regression analysis. A correlation coefficient (R) is generated in the analysis which ranges in value from -1.0 (a perfect negative linear correlation) to 1.0 (a perfect positive linear relationship). A zero value indicates no linear relationship exists. If a strong linear relationship exists, linear

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regression analysis should be used to evaluate the data sets. If a non-linear relationship exists, a non-linear regression analysis may be considered.

3.3 Linear Regression Analysis

Regression analysis is used to fit a model between the independent variable (field data) and the dependant variable (laboratory data) to determine if a linear relationship exists and if that relationship is significant. Regression analysis yields the coefficient of determination (R-square), which defines the proportional amount of variability explained by the regression model. The R-square value ranges from 0.0, which means no variability to 1.0, which indicates that 100-percent of the variability is explained by the model. The regression also yields the F statistic, which determines if the model explains a significant amount of the variation in the data sets. A p-value may also be generated for the F statistic. If the p-value for the F statistic is less than the significance level (0.05), and the R-square value is high (> 0.7), the regression model is significant.

The residuals of the regression model should be examined for potential outliers. The residuals are the differences between the predicted dependent values and the actual dependent values. A plot of residuals versus dependent values should be a random scattering of points. Anomalies or potential outliers are usually apparent. If any potential outliers are present, the regression analysis should be performed without these values to determine their impact upon the model. If the sample size for regression is small (less than 8 observations) removal of data points should be avoided, irrespective of their impact, because their removal greatly increases the error associated with the regression analysis.

4 Mercury Comparison Studies

Real-time and laboratory analytical data collected from August 2001 through December 2002 were statistically evaluated to determine comparability of NIOSH vs. time averaged Lumex or Tracker mercury vapor readings. The Lumex and Tracker real-time mercury analyzers were factory calibrated. Lumex values (ng/m^3) were converted to $\mu\text{g}/\text{m}^3$ by dividing by 1000 prior to comparison with NIOSH values. Data for the following studies were evaluated:

Lumex vs. NIOSH; 106 observations

Lumex vs. NIOSH; NIOSH $\square 10 \mu\text{g}/\text{m}^3$; 100 observations

Lumex vs. NIOSH; NIOSH $\square 1 \mu\text{g}/\text{m}^3$; 62 observations

Tracker vs. NIOSH; 156 observations

Tracker vs. NIOSH; NIOSH $\square 10 \mu\text{g}/\text{m}^3$; 125 observations

Tracker vs. NIOSH; NIOSH $\square 1 \mu\text{g}/\text{m}^3$; 42 observations

4.1 Evaluation of Mercury Data

All pairwise comparisons, correlation, and regression analysis evaluations were performed using the SASTM (V 8.0) statistical analysis software package. Data plots were done using Corel Quattro Pro (V 8) and Corel Presentations (V 10). The SASTM correlation analysis output includes two coefficients: the Pearson coefficient for normal (bell shaped) data distributions and the Spearman coefficient for non-normal distributions. The SASTM regression output includes a Student Residual and Cook's D value for each

observation (Schlotzhauer and Little, 1987). The Student Residual is the residual divided by the standard error. The Cook's D value is a relative measure of data quality. If the Student Residual is between 2.0 and 3.0 in absolute value, the observation may be an outlier. If it is 3.0 or larger in absolute value, the observation is considered a probable outlier. When the Student Residual is larger than 2.0 in absolute value and Cook's D is outside the range of the data set, the observation may be considered a potential outlier and a new regression analysis should be performed without that observation.

4.2 Statistical Analysis Results

Figures 1 and 2 show laboratory (NIOSH) vs real-time (Lumex or Tracker) data. In general, pairwise comparisons analysis indicated that the data were not normally distributed and there was a significant difference between real-time and NIOSH data sets. The correlation coefficients indicated that the data were highly correlated and regression analysis was justified.

Regression analysis results for Lumex vs NIOSH data sets are presented in Table 1. Results without potential outliers showed that Lumex and NIOSH data were comparable. The slopes for the regressions showed that Lumex readings were low compared to laboratory analysis (about 1/2 the NIOSH value). The RMS error (0.011) and slope (1.975) for Lumex vs. NIOSH \square 1 indicated that corrected Lumex results of about 0.022 $\mu\text{g}/\text{m}^3$ or greater were comparable to laboratory analysis.

Regression analysis results for Tracker vs NIOSH data sets are presented in Table 2. Results without potential outliers showed that the data were highly comparable. The RMS error 0.054 for Tracker vs. NIOSH \square 1 indicated that Tracker results of about 0.1 $\mu\text{g}/\text{m}^3$ or greater were comparable to laboratory analysis results. The slopes for the regressions indicated that Tracker readings were in agreement with laboratory analysis.

5 Real-Time Analyzer Calibration Studies

Statistical analysis showed a significant difference between NIOSH 6009 and real-time instrumentation results. In order to verify this difference, a Hg gas standard with a certified concentration of 5.0 $\mu\text{g}/\text{m}^3$ was obtained (Spectra Gases, Branchburg, NJ) and the Hg concentration was measured using real-time instrumentation as shown in Figure 3. The Hg gas from the cylinder was analyzed with the real-time analyzers to check/verify real-time readings. Time averaged readings were used to determine percent recovery of the standard gas concentration for the individual real-time mercury analyzer. A correction factor, based on percent recovery, was then used to calculate a new calibration factor for the analyzer. The new calibration factor was entered into the analyzer's memory to adjust real-time readings to agree with the Hg gas standard concentration (5 $\mu\text{g}/\text{m}^3$). The Hg gas from the cylinder was also analyzed using the NIOSH method to check/verify the cylinder concentration. The NIOSH results (5.05 and 4.97) were in excellent agreement with the certified mercury concentration (5.0 $\mu\text{g}/\text{m}^3$).

Two Tracker units (Tracker#1 and Tracker#2) and three Lumex units (Lumex#1, Lumex#2, and Lumex#3) were calibrated with the standard Hg gas. After calibration, real-time and laboratory analytical data collected during March 2003 were statistically evaluated to determine comparability of NIOSH vs. time averaged Lumex or Tracker mercury vapor

readings. Data for the following studies were evaluated:

Tracker#1 vs. NIOSH; 33 observations

Tracker#1 vs. NIOSH; NIOSH $\leq 1 \mu\text{g}/\text{m}^3$; 25 observations

Tracker#2 vs. NIOSH; 33 observations

Tracker#2 vs. NIOSH; NIOSH $\leq 1 \mu\text{g}/\text{m}^3$; 17 observations

Lumex#1 vs. NIOSH; 15 observations

Lumex#1 vs. NIOSH; NIOSH $\leq 1 \mu\text{g}/\text{m}^3$; 6 observations

Lumex#2 vs. NIOSH; 10 observations

Lumex#2 vs. NIOSH; NIOSH $\leq 1 \mu\text{g}/\text{m}^3$; 7 observations

Lumex#3 vs. NIOSH; 4 observations

5.1 Statistical Analysis Results

Figures 4 - 7 show NIOSH vs calibrated real-time Hg analyzer (Lumex or Tracker) data. In general, pairwise comparisons analysis indicated that Tracker vs NIOSH data sets were not normally distributed and there was a significant difference between the data sets. Pairwise comparisons for Tracker#2 vs NIOSH, where the NIOSH value was less than or equal to $1.0 \mu\text{g}/\text{m}^3$, indicated that the data were not normally distributed and were not significantly different. The correlation coefficients indicated that the data were highly correlated and regression analysis was justified. Pairwise comparisons indicated that Lumex#1 or Lumex#2 vs NIOSH data were normally distributed and the data sets were significantly different. The correlation coefficients indicated that the data were highly correlated and regression analysis was justified. Pairwise comparisons and correlation analysis were not feasible for Lumex#3 vs NIOSH data due to the small sample size.

Regression analysis results without potential outliers (Table 3) showed that time averaged Hg analyzer and NIOSH data were highly comparable. The RMS errors (0.011 - 0.028) for Lumex Vs. NIOSH ≤ 1 indicated that Lumex results of about $0.03 \mu\text{g}/\text{m}^3$ or greater were comparable to laboratory analysis results. The RMS errors (0.034- 0.042) for Tracker vs. NIOSH ≤ 1 indicated that Tracker results of about $0.1 \mu\text{g}/\text{m}^3$ or greater were comparable to laboratory analysis. Regression results for small sample size ($n < 7$) should be viewed as exploratory. The slopes for the regressions showed that readings for calibrated real-time Hg analyzers were in agreement with laboratory analysis.

6 Conclusions

Statistical analysis indicated that field (Lumex or Tracker) and laboratory (NIOSH 6009) data for analysis of mercury in air samples were comparable for Lumex and Tracker Hg readings of about 0.03 and $0.1 \mu\text{g}/\text{m}^3$ or greater, respectively, provided that the factory calibrations of the real-time analyzers were adjusted based on the mercury concentration measured from a standard mercury gas source in a laboratory environment. Based on statistical analysis, Lumex and Tracker field analyzers provide real-time screening to assess initial extent of metallic mercury contamination, to identify "hot spots", and to monitor progress of decontamination procedures at a spill site. In order to meet final clean-up action levels (0.3 - $1.0 \mu\text{g}/\text{m}^3$) for indoor mercury spills, time averaged Lumex and Tracker results may be used instead of the NIOSH method under certain circumstances, such as during emergency responses, depending on site requirements. Additional work is in progress to

define the conditions when real-time metallic mercury vapor monitoring instruments, such as the Lumex or Tracker, may be used.

7 Acknowledgments and Disclaimer

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Table 1. Regression Analysis Results for Mercury Comparison Studies,
NIOSH (dependent) vs. Lumex (independent)

Parameter	Lumex vs. NIOSH; All Data		Lumex vs. NIOSH; NIOSH \square 10		Lumex vs. NIOSH; NIOSH \square 1	
	All Data	Without Potential Outliers	All Data	Without Potential Outliers	All Data	Without Potential Outliers
n	106	101	100	91	62	55
R-square	0.9704	0.9898	0.9843	0.9958	0.9365	0.9530
slope	1.794	1.816	1.909	1.969	1.877	1.975
intercept	0.187	0.089	0.03	0.018	0.028	0.011
RMS error	0.73	0.28	0.25	0.12	0.069	0.032
F-value (p-value)	3408 (<0.0001)	9615 (<0.0001)	6159 (<0.0001)	21150 (<0.0001)	885 (<0.0001)	1074 (<0.0001)

Table 2. Regression Analysis Results for Mercury Comparison Studies,
NIOSH (dependent) vs. Tracker (independent)

Parameter	Tracker vs. NIOSH; All Data		Tracker vs. NIOSH; NIOSH \square 10		Tracker vs. NIOSH; NIOSH \square 1	
	All Data	Without Potential Outliers	All Data	Without Potential Outliers	All Data	Without Potential Outliers
n	156	150	125	124	42	35
R-square	0.9687	0.9882	0.4416	0.9265	0.8527	0.9523
slope	1.19	1.183	0.456	1.149	1.098	1.076
intercept	-0.138	0.163	1.73	0.153	0.037	0.031
RMS error	5.29	1.57	1.98	0.71	0.1	0.054
F-value (p-value)	4767 (<0.0001)	12438 (<0.0001)	97 (<0.0001)	1539 (<0.0001)	231 (<0.0001)	659 (<0.0001)

Regression results based on factory calibration for Lumex and Tracker analyzers

n = number of observations

R-square (r^2) = coefficient of determination for the regression model

RMS error = the standard error of the Y estimate for the regression model

Table 3. Regression Analysis Results for Real-Time Analyzer Calibration Studies, NIOSH
(dependent) vs. Lumex or Tracker (independent)

Lumex vs. NIOSH					
Parameter	Lumex#1 All Data	Lumex#1 NIOSH □ 1	Lumex#2 All Data	Lumex#2 NIOSH □ 1	Lumex#3 All Data
n	15	6	9	7	4
R-square	0.9957	0.9982	0.9989	0.9501	0.9987
slope	1.24	1.254	0.9698	1.071	1.362
intercept	0.019	-0.015	-0.021	-0.068	-0.07
RMS error	0.101	0.011	0.028	0.028	0.018
F-value (p-value)	2981 (<0.0001)	2160 (<0.0001)	6109 (<0.0001)	95 (0.0002)	1545 (0.0006)

Tracker vs. NIOSH				
Parameter	Tracker#1 All Data	Tracker #1 NIOSH □ 1	Tracker#2 All Data	Tracker#2 NIOSH □ 1
n	32	23	33	14
R-square	0.9886	0.9594	0.9937	0.9802
slope	1.144	1.062	1.117	1.109
intercept	-0.034	0.008	-0.021	-0.021
RMS error	0.071	0.042	0.096	0.034
F-value (p-value)	2596 (<0.0001)	497 (<0.0001)	4866 (<0.0001)	595 (<0.0001)

Regression results excluding potential outliers based on laboratory calibration
for Lumex and Tracker analyzers
n = number of observations
R-square (r^2) = coefficient of determination for the regression model
RMS error = the standard error of the Y estimate for the regression model

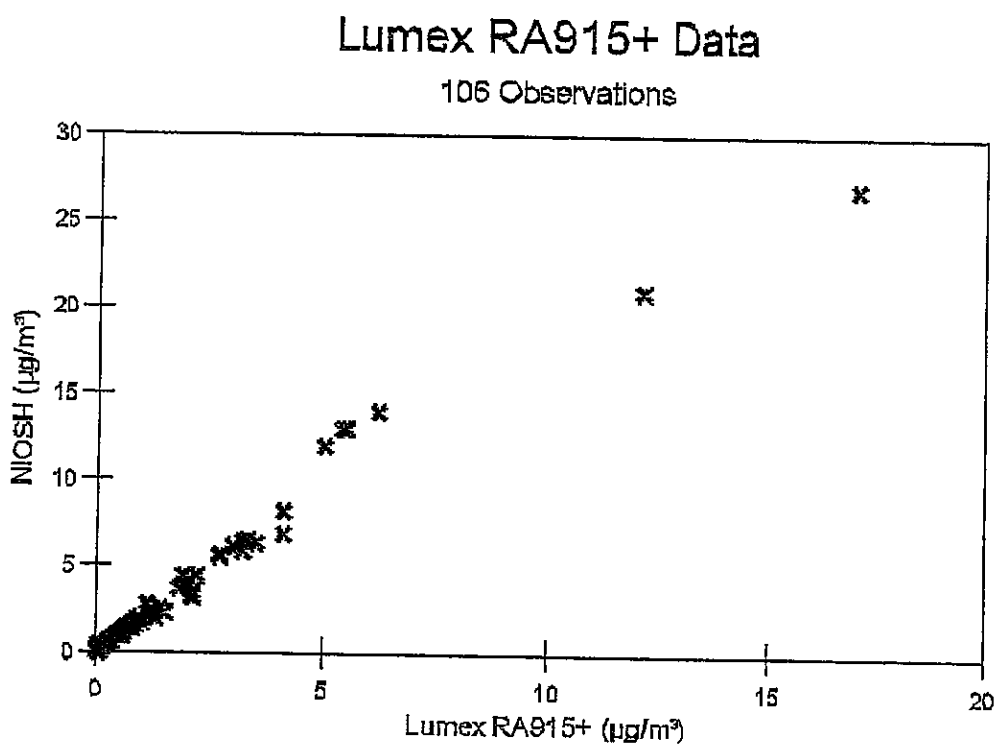
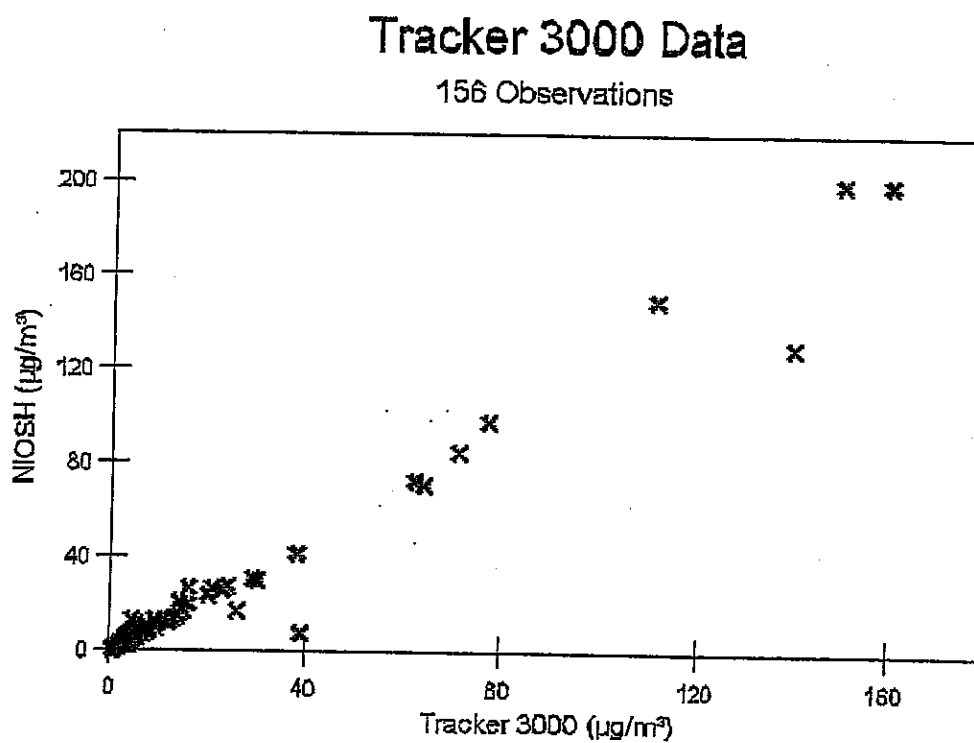


Figure 1. Laboratory (NIOSH 6009) and Field (Lumex RA915+) Mercury Results



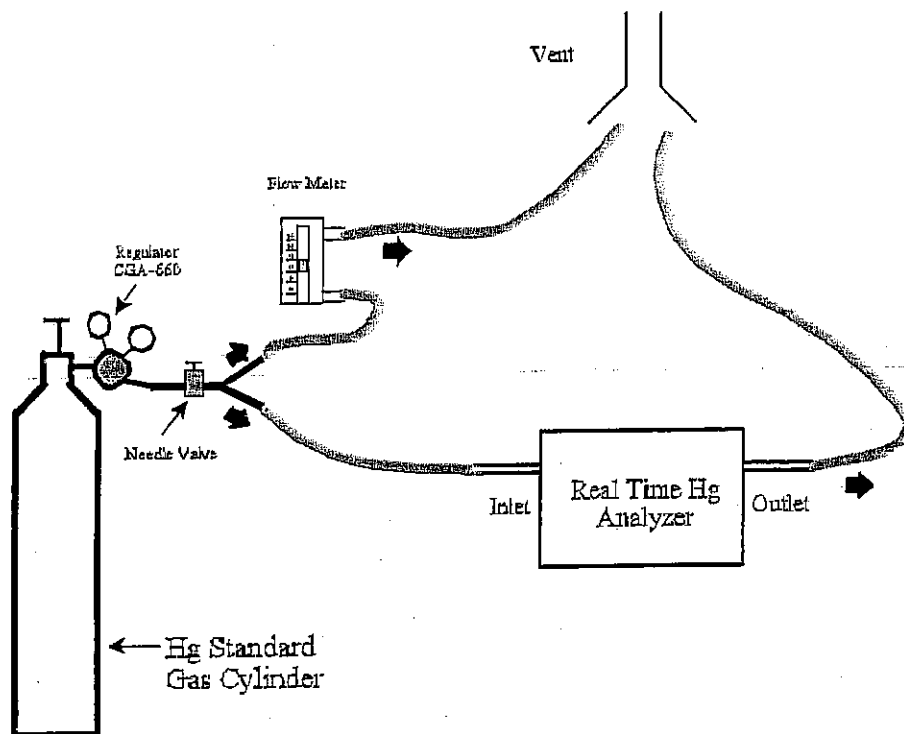


Figure 3. Setup for Calibrating Real-Time Mercury Analyzers

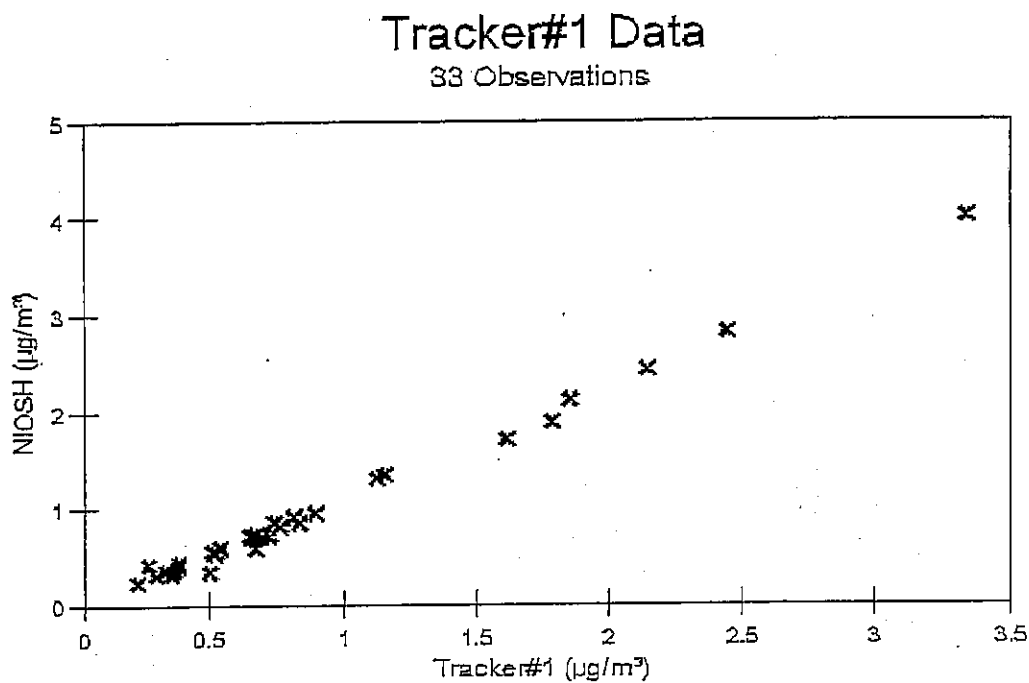


Figure 4. Laboratory and Tracker#1 (Calibrated) Mercury Results

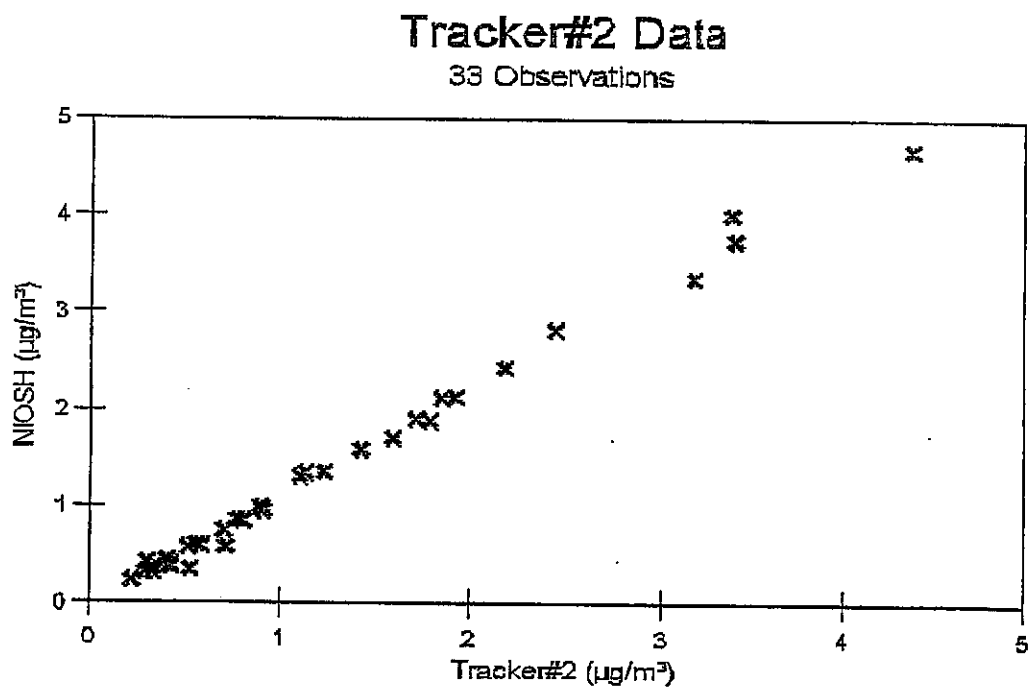


Figure 5. Laboratory and Tracker#2 (Calibrated) Mercury Results

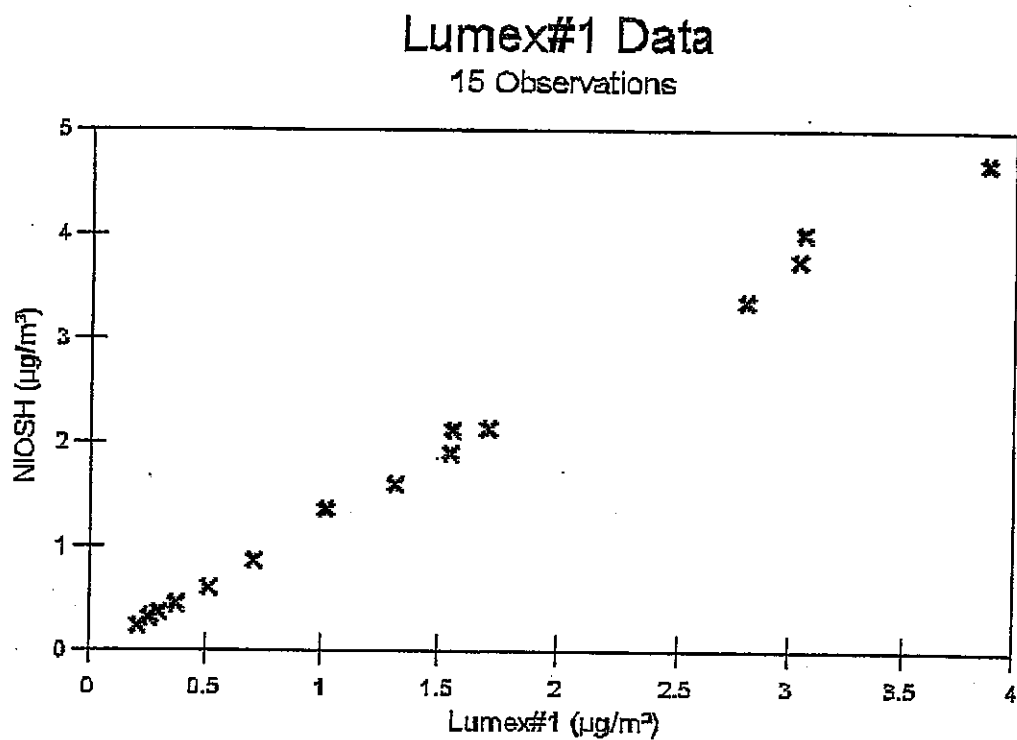


Figure 6. Laboratory and Lumex#1 (Calibrated) Mercury Results

Lumex#2 Data

10 Observations

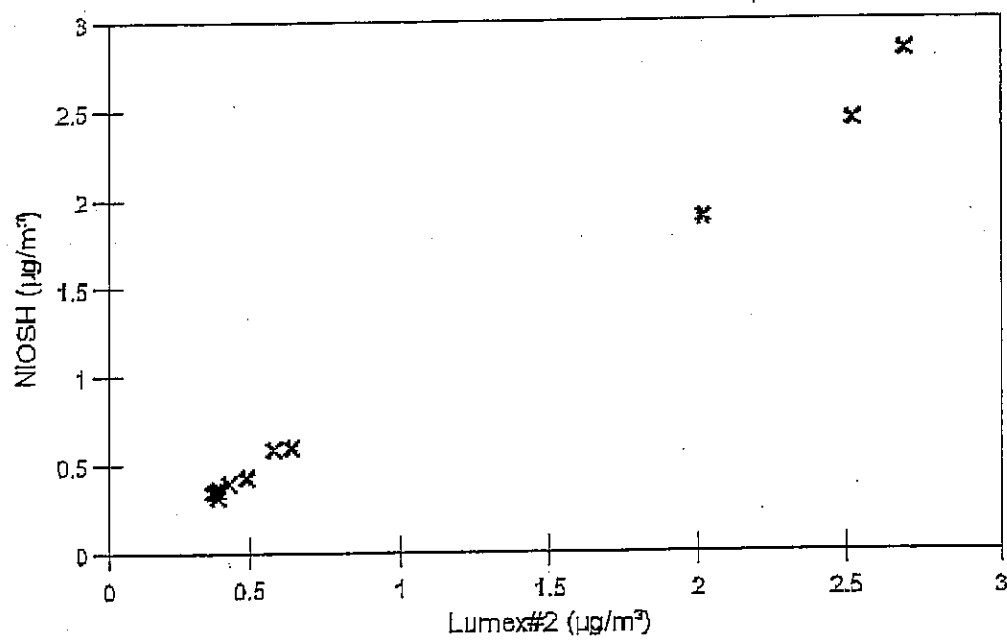


Figure 7. Laboratory and Lumex#2 (Calibrated) Mercury Results

APPENDIX D

Comparison of Methods for Mercury Analysis

Comparison of Methods for Mercury Analysis

Method Number	Last Revision Date	Agency	Sample Matrix	Typically-Achievable Detection Limit	Method of Detection	Notes
SW-846 7470A	September 1994	USEPA, Office of Solid Wastes	extracts, aqueous samples, ground water	0.2 ug/L (ppb)	atomic absorption spectrometry of mercury vapor ('cold-vapor AA', or CVAA)	
SW-846 7471A	September 1994	USEPA, Office of Solid Wastes	solid or semisolid wastes	0.2 ug/L or ug/Kg (ppb)	CVAA	This method is equivalent to Method 7470A, except for an added step to digest the solid sample with acid
1631E	November 2002	USEPA, Office of Water	water and wastewater	0.2 ng/L (ppt)	cold-vapor atomic fluorescence spectrometry (CVAFS)	Typically used when Clean Water Act NPDES permit requires measurement of mercury concentrations in the 0.5-100 ng/L range
245.7	January 2001	USEPA, Office of Water	'drinking water, surface and ground waters, marine water, and industrial and municipal wastewater'	1.8 ng/ L (ppt)	CVAFS	Similar to Method 1631, except that 245.7 uses liquid-gas separation and a dryer tube for analyte isolation, while Method 1631 uses a purge and gold trap isolation procedure.
6009	August 1994	NIOSH	air sample in sorbent tube	0.01 mg/M ³ (10 L air sample)	CVAA	

APPENDIX E

SOP for Modified NIOSH Method 6009



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 1 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

CONTENTS

- 1.0 SCOPE AND APPLICATION
- 2.0 SUMMARY OF METHOD
- 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE
- 4.0 INTERFERENCES AND POTENTIAL PROBLEMS
- 5.0 EQUIPMENT/APPARATUS
 - 5.1 Atomic Absorption Spectrophotometer
 - 5.2 Strip-Chart Recorder or Integrator
 - 5.3 Glassware
- 6.0 REAGENTS
 - 6.1 Type I Water (ASTM D1193)
 - 6.2 Concentrated Nitric Acid (HNO_3)
 - 6.3 Concentrated Hydrochloric Acid (HCl)
 - 6.4 Stock Mercury Solutions
 - 6.5 Stannous Chloride, 10% in 1:1 HCl *
 - 6.6 Calibration Standards*
- 7.0 PROCEDURE
 - 7.1 Sample Preparation
 - 7.2 Calibration Standards*
 - 7.3 Method Blank



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 2 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

CONTENTS (Cont'd)

- 7.4 Laboratory Control Standard
- 7.5 Calibration Verification Standards
- 7.6 Method Detection Limit Standard
- 7.7 Blank Spike/Blank Spike Duplicate*
- 7.8 Lot Blank
- 7.9 Trip Blank
- 7.10 Field Blanks
- 7.11 AA Calibration and Measurement
- 8.0 CALCULATIONS
- 9.0 QUALITY ASSURANCE/QUALITY CONTROL
 - 9.1 Initial Calibration/Calibration Check
 - 9.2 Method Detection Limit*
 - 9.3 Continuing Calibration Verification
 - 9.4 Blanks
 - 9.5 BS/BSD Samples
 - 9.6 Dilution Analysis
- 10.0 DATA VALIDATION
- 11.0 HEALTH AND SAFETY
- 12.0 REFERENCES
- 13.0 APPENDIX
 - A - NIOSH Method 6009

* This section affected by Revision 2.0



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 3 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

SUPERCEDES: SOP #1827; Revision 1.0; 01/16/96.

1.0 SCOPE AND APPLICATION

This method is a modification of NIOSH Method 6009 for mercury (Appendix A). It is applicable to the analysis of indoor air samples of volatilized elemental mercury (Hg) collected on solid sorbent material (typically Hopcalite) contained in glass collection tubes. The sorbent sample is digested and the Hg concentration is determined by the cold-vapor Atomic Absorption (AA) spectroscopy technique. The method is simple, rapid, and relatively free of matrix interferences.

Detection limits, sensitivity, and optimum ranges for Hg analysis will vary with the sorbent material, volume of air sampled, and models of atomic absorption spectrophotometers used.

This standard operating procedure may be varied or changed as required, depending upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed will be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

2.0 SUMMARY OF METHOD

Indoor air samples of elemental Hg are collected on solid Hopcalite sorbent material contained in glass tubes. Air is pumped through the sorbent with a personal sampling pump which can be programmed for collection time and flowrate [typically 0.25 to 0.5 liters per minute (L/min)]. Pump flow rate is initially calibrated against a rotameter reference and is checked before/after sample collection. Sampling stations are typically set up in several locations within the residence with duplicate stations in areas suspected of high level contamination. Refer to manufacturer's instructions for proper setup and operation of sampling equipment and ERT/REAC SOP #2119, *Air Sampling for Metals*.



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 4 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

The sorbent material from the collection tube (typically 200 mg in a single section) is quantitatively transferred to a 100-milliliter (mL) volumetric flask. The sample is digested by first adding 2.5 mL of concentrated nitric acid followed by 2.5 mL of concentrated hydrochloric acid. After digestion is complete, the sample is diluted to volume with deionized water.

The sample is analyzed by the cold-vapor AA spectroscopy technique with no additional dilutions. The principle is essentially the same as direct aspiration AA, except a cold-vapor generator system, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Sample holding times, suggested collected volume, preservative, and type of containers are as follows:

Holding Measurement	Collection Volume Req. (L)	Type of Containers	Preservative	Time
<u>Mercury in air:</u>				
Solid Hopcalite sorbent	10 - 200 L ⁽¹⁾	sorbent tube	sorbent tube, 25° C	30 days

⁽¹⁾ The volume of air collected is directly related to detection limit; the larger the volume, the lower the detection limit.



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 5 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 6 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Although the method minimizes dilution and sample matrix effects, the technique is not completely interference free. Inorganic and organic Hg compounds may cause a positive interference

Cross-contamination and contamination of the sample can be major sources of error because of the sensitivities achieved with the cold-vapor AA spectroscopy technique. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Section 5.3. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results.

5.0 EQUIPMENT/APPARATUS

5.1 Atomic Absorption Spectrophotometer

A single- or dual-channel, single- or double-beam instrument having a grating monochromator, Hg hollow cathode lamp, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nanometers (nm), and provisions for interfacing with a strip-chart recorder or computer, printer, autosampler, and Hg cold-vapor generation system.

5.2 Strip-Chart Recorder or Integrator

A recorder is useful to provide a permanent record and for easy recognition of any problems with the analysis.

5.3 Glassware

All glassware, polypropylene, or TeflonTM containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and Type I water. If it can be documented through an active analytical quality control program, using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 7 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

eliminated from the procedure.

6.0 REAGENTS

All reagents and standard solutions are prepared and documented in accordance with ERT/REAC SOP #1012, *Preparation of Standard Solutions*.

6.1 Type I Water (ASTM D1193)

Use Type I water for the preparation of all reagents and calibration standards and as dilution water.

6.2 Concentrated Nitric Acid (HNO_3)

Use commercially available high-purity, spectrograde acid certified for AA use.

6.3 Concentrated Hydrochloric Acid (HCl)

Use commercially available high-purity, spectrograde acid certified for AA use.

6.4 Stock Mercury Solutions

Use a commercially available Hg standard solution or prepare a 1000 micrograms per milliliter ($\mu\text{g/mL}$) stock standard solution from high purity mercuric oxide (HgO) using Type I water and redistilled HCl . Dissolve 1.0798 grams (g) of dry HgO in 50 mL of 1:1 HCl , then dilute to one liter (1 L) with Type I water.

6.5 Stannous Chloride, 10% in 1:1 HCl

Dissolve 20 grams (g) reagent grade stannous chloride in 100 mL concentrated HCl . Slowly add this solution to 100 mL Type I water and mix well. Prepare fresh daily or each time calibration standards are prepared.



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 8 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

6.6 Calibration Standards

For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. For best results, intermediate and working standards should be prepared fresh each time a batch of samples is analyzed. A blank and a minimum of three working standards in the linear part of the calibration range should be used to calibrate the AA instrument.

Prepare all calibration and all check standards using the procedures outlined in Section 7.0. All QC solutions are prepared by spiking blank sorbent media. This matches the sample matrix and, thereby, minimizes sample matrix effects.

7.0 PROCEDURE

7.1 Sample Preparation

1. Quantitatively transfer the Hopcalite sorbent and the front glass wool plug from each sampler tube into a 100-mL volumetric flask.
2. Add 2.5 mL of concentrated HNO_3 followed by 2.5 mL concentrated HCl .

NOTE: The Hg must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.

3. Allow the sample to stand for 1 hour or until the black Hopcalite sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
4. Carefully dilute to 100 mL with Type I water.
5. The final sample solution (blue to blue-green in color) contains 2.5 percent HNO_3 , 2.5 percent HCl , and is analyzed for Hg with no additional dilution (except for samples containing high concentrations of Hg).



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 9 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

7.2 Calibration Standards

Prepare a blank, and a minimum of three working standards in graduated amounts in the linear part of the calibration range (0.2 to 10.0 $\mu\text{g/L}$) by spiking blank sorbent media (from unused Hopcalite tubes) with known amounts of Hg. Dissolve the blank sorbent media, using steps 1 - 3 of the procedure outlined in Section 7.1. Spike each standard solution with the appropriate amount of Hg, and dilute to volume per step 4 of the procedure outlined in Section 7.1.

7.3 Method Blank

Prepare the method blank (reagent blank) from blank sorbent media. Prepare the method blank using the procedure outlined in Section 7.1 at the same time the samples are prepared. A minimum of one method blank per batch of 20 samples or less must be prepared.

7.4 Laboratory Control Standard

Prepare the laboratory control standard (LCS) by spiking blank sorbent media with a known amount of Hg (at or near midrange of the calibration curve). Use an independent source of Hg (different than that used to prepare calibration standards) for the LCS sample. Prepare the LCS sample using the procedure outlined in Section 7.1 at the same time the samples are prepared.

7.5 Calibration Verification Standards

Prepare initial calibration verification (ICV) and continuing calibration verification (CCV) standards by spiking blank sorbent media with known amounts of Hg (at or near midrange of the calibration curve). Prepare ICV and CCV standards using the procedure outlined in Section 7.1.

7.6 Method Detection Limit Standard



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 10 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

Prepare the method detection limit (MDL) standard by spiking blank sorbent media with a known amount of Hg at the expected MDL (typically half the concentration of the lowest calibration standard). Prepare the MDL standard using the procedure outlined in Section 7.1.

7.7 Blank Spike/Blank Spike Duplicate

Prepare blank spike (BS) and blank spike duplicate (BSD) samples by spiking blank sorbent media with known amounts of Hg (5 to 10 times the detection limit). Spike blank sorbent media with appropriate amounts of Hg and prepare BS/BSD samples using the procedure outlined in Section 7.1. BS/BSD samples are prepared in the laboratory to monitor precision and accuracy of the method.

Use the BS/BSD samples delivered to the laboratory with unknown samples, or blank tubes from the same lot if none are provided with the samples.

7.8 Lot Blank

One unopened sampling tube must be prepared and analyzed as a lot blank with each sample lot of twenty tubes or less per project. The lot blank tube is delivered to the laboratory with the samples, broken up without disturbing the contents, and then prepared using the procedure outlined in Section 7.1.

7.9 Trip Blank

One blank tube from the same lot is included as the trip blank. The tube is broken and carried to the site in the same type of container as the samples. It is delivered to the laboratory with the samples and is prepared using the procedure outlined in Section 7.1.

7.10 Field Blanks

One or more blank tubes from the same lot are included as field blanks. The tube is broken and carried to the sampling stations at the site but no air is sampled. Field blanks



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 11 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

are delivered to the laboratory with the samples and are prepared using the procedure outlined in Section 7.1.

7.11 AA Calibration and Measurement

Differences between the various makes and models of satisfactory AA instruments and cold-vapor generators prevent the formulation of detailed instructions applicable to each system. The analyst should follow the manufacturer's operating instructions for a particular instrument and cold-vapor generator system.

Analyze the working standards together with the samples and blanks. Analyze the full set of working standards at the beginning of the run to establish the initial calibration curve. Analyze additional standards during sample analysis to confirm instrument response (see Section 9.0).

Samples with a high concentration of Hg should be diluted into the linear calibration range (see Section 9.6).

8.0 CALCULATIONS

For determination of concentration, read the Hg value (B) in $\mu\text{g/L}$ from the calibration curve or directly from the read-out system of the instrument. Calculate the concentration of Hg in the sample aliquot (A) as follows:

$$A = \mu\text{g/L Hg in sample aliquot} = B \frac{D + C}{D}$$

where:

B = Concentration of Hg from the calibration curve ($\mu\text{g/L}$)
C = Amount of acid blank matrix used for dilution (mL)
D = Sample aliquot used for dilution (mL)



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 12 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

Note: If no dilution was required, $C = 0$, and $A = B$.

Calculate the amount of Hg (W) for each Hopcalite tube:

$$W = \mu\text{g/tube Hg} = A (0.1)$$

where:

A = Concentration of Hg in the sample aliquot ($\mu\text{g/L}$)
 0.1 = Final solution volume (L/tube)

Calculate the concentration ($\mu\text{g/m}^3$) of Hg in the air volume sampled:

$$\mu\text{g/m}^3 \text{ Hg} = 1000 \frac{W - BLK}{V}$$

where:

W = Amount of Hg in each Hopcalite tube ($\mu\text{g/tube}$)
 BLK = Amount of Hg present in the method blanks ($\mu\text{g/tube}$)
 V = Volume of air sampled (L/tube)

NOTE: Report $\mu\text{g/tube}$ results for lot blank, trip blank, field blank(s), and BS/BSD samples because no air volume is collected for these samples.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

All quality control data should be documented and available for reference or inspection.

9.1 Initial Calibration/Calibration Check

A calibration curve must be prepared each day with a minimum of a blank and three



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 13 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

standards (Sections 7.2 and 7.11). The initial calibration must be verified by analysis of the method blank (Section 7.3), the ICV standard (Section 7.5), and the LCS sample (Section 7.4). The ICV and LCS results must be within ± 10 percent of the true value.

9.2 Method Detection Limit

The MDL standard (Section 7.6) must be analyzed at the beginning and end of sample analysis to verify the Hg MDL. MDL standard results must be within ± 20 percent of the true value. The MDL is $0.10 \mu\text{g/L}$ ($0.05 \mu\text{g/m}^3$ for a 200-L air sample) using a Varian Spectra AA-300TM equipped with a VGA-76 vapor generator accessory.

9.3 Continuing Calibration Verification

If 20 or more samples per day are analyzed, the working standard curve must be verified by analyzing the method blank and the CCV standard after every 10 samples. CCV results must be within ± 10 percent of the true value.

9.4 Blanks

One lot blank, one trip blank, and a minimum of one field blank must be prepared and analyzed with each sample lot.

9.5 BS/BSD Samples

At least one BS and one BSD sample should be analyzed after every 10 samples or with each sample lot to verify precision and accuracy of the method.

BS/BSD percent recovery (%R) should be within 75-125 percent (advisory only) and calculated as:

$$\%R = \frac{(R - BLK)}{SL} \times 100$$



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 14 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

where:

R = BS or BSD sample result ($\mu\text{g}/\text{tube}$)
 BLK = Amount of Hg present in the lot blank ($\mu\text{g}/\text{tube}$)
 SA = Spike added ($\mu\text{g}/\text{tube}$)

The Relative Percent Difference (RPD) for duplicate samples should be within 80-120 percent (advisory only) and calculated as:

$$RPD = \frac{(S - D)}{(S + D)/2} \times 100$$

where:

S = BS sample result
 D = BSD sample result

9.6 Dilution Analysis

If the Hg concentration of any sample exceeds the initial calibration range, that sample must be diluted and reanalyzed. Use the results of the original analysis to determine the approximate dilution factor required to get a Hg concentration within the upper half of the initial linear calibration range. Analyze the diluted sample aliquot. Adjust the dilution factor if the Hg concentration is not within the desired range. Report results for the diluted aliquot with the smallest dilution factor which produces a Hg concentration in the upper half of the linear calibration range (see Section 8.0).

10.0 DATA VALIDATION

Data is considered valid if all the procedures for analyzing Hg in air are followed and QA/QC criteria are met.

11.0 HEALTH AND SAFETY



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 15 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for following the chemical hygiene plan and laboratory safety program regarding the safe handling of the chemicals specified in this method.

When working with potentially hazardous materials, refer to U.S. EPA, Occupational Safety and Health Administration (OSHA) and corporate health and safety practices. More specifically, refer to ERT/REAC SOP #3013, *REAC Laboratory Safety Program*.

12.0 REFERENCES

Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency. September, 1986. *Test Methods for Evaluating Solid Waste*. Third Edition. SW-846.

NIOSH Manual of Analytical Methods, Method 6009, Mercury. August 15, 1994. Issue 2.

ERT/REAC SOP #1818, *Determination of Metals by Atomic Absorption (AA) Methods*.

ERT/REAC SOP #2119, *Air Sampling for Metals, [NIOSH METHOD 7300, Elements]*



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 16 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

FORMULA: Hg

MERCURY

M.W.: 200.59

METHOD: 6009
ISSUED: 5/15/89

OSHA: 0.05 mg/m³ (skin)
NIOSH: 0.05 mg/m³ (skin) [1]
ACGIH: 0.05 mg/m³

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP
356 °C; MP -39 °C; VP 0.16 Pa
(0.0012 mm Hg; 13.2 mg/m³) @ 20 °C

SYNONYMS: quicksilver; CAS# 7439-97-6.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (Hydrar in single section, 200 mg)	! TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR !
FLOW RATE: 0.15 to 0.25 L/min	! ANALYTE: elemental mercury !
VOL-MIN: 2 L @ 0.05 mg/m ³ -MAX: 100 L	! DESORPTION: conc. HNO ₃ /HCl @ 25 °C, dilute ! to 50 mL !
SHIPMENT: routine	! WAVELENGTH: 253.7 nm !
SAMPLE STABILITY: 30 days @ 25 °C [2]	! CALIBRATION: standard solutions of Hg ⁺⁺ ! in 1% HNO ₃ !
FIELD BLANKS: 10% of samples MEDIA BLANKS: at least 3 per set	! RANGE: 0.1 to 1.2 µg per sample !
	! ESTIMATED LOD: 0.03 µg per sample !
	! PRECISION (s _r): 0.042 @ 0.9 to 3 µg per ! sample [4] !
ACCURACY	!
RANGE STUDIED: 0.002 to 0.8 mg/m ³ [3] (10-L samples)	!
BIAS: not significant [2,3]	!
OVERALL PRECISION (s _p): not determined	!
APPLICABILITY: The working range is 0.01 to 0.5 mg/m ³ for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [4].	
INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.	
OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [5,6,7]. This method is based on the method of Rathje and Marcero [8] and is similar to the OSHA method ID 145H [3].	



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 17 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

MERCURY

METHOD: 6009

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO₃), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg⁺⁺, 1000 µg/mL. Commercially available or dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloric acid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 µg/mL. Place 0.1 mL 1000 µg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v).

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hydrar held in place by glass wool plugs (commercially available from SKC, Inc., Cat. #226-17-1).
NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the Hydrar may be used if particulate mercury is to be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.
4. Strip chart recorder.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-µL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

*See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and intact skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.15 to 0.25 L/min for a sample size between 2 and 100 L.
NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hydrar sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO₃ followed by 2.5 mL conc. HCl.
NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 hour or until the black Hydrar sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in the BOD bottle must be 100 mL. To prevent possible loss of mercury during transfer, place the pipet tip below the surface of the liquid in the BOD bottle.



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 18 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

METHOD: 6009

MERCURY

CALIBRATION AND QUALITY CONTROL:

10. Prepare a minimum of two series of working standards covering the range 0.01 to 0.5 μg Hg per aliquot by adding known amounts of the intermediate standard to BOD bottles containing enough 1% nitric acid to bring the final volume to 100 mL.
11. Analyze the working standards together with the samples and blanks (steps 13 through 16). Analyze full set of standards at the beginning of the run, and a second set at the end of the run. Additional standards may be run intermediately during the analysis to confirm instrument response.
12. Prepare calibration graph (peak height from the recorder vs. solution concentration, $\mu\text{g}/\text{sample}$).

MEASUREMENT:

13. Zero the spectrophotometer by removing the bubbler from the BOD bottle, allowing the baseline on the recorder to stabilize.
14. Place the bubbler in a BOD bottle containing 0.5 μg mercury in 100 mL 1% nitric acid. Adjust the spectrophotometer so that it will give a 75% to full-scale deflection of the recorder.
15. Vent the mercury vapor from the system.
16. Analyze standards, samples and blanks (including media blanks).
 - a. Remove the bubbler from the BOD bottle.
 - b. Rinse the bubbler with deionized water.
 - c. Allow the recorder tracing to establish a stable baseline.
 - d. Remove the stopper from the BOD bottle containing the next sample to be analyzed. Gently swirl the BOD bottle.
 - e. Quickly add 5 mL 10% stannous chloride solution.
 - f. Quickly place the bubbler into the BOD bottle.
 - g. Allow the spectrophotometer to attain maximum absorbance.
 - h. Vent the mercury vapor from the system.
 - i. Rinse the bubbler using deionized water.
 - j. Place the bubbler into an empty BOD bottle. Continue venting the mercury until a stable baseline is obtained.
 - k. Close the mercury vent.

CALCULATIONS:

17. Calculate the amount of mercury in the sample aliquot ($W, \mu\text{g}$) from the calibration graph.
18. Calculate the concentration C (mg/m^3), of mercury in the air volume sampled, V (L):

$$C = [W \cdot (V_s/V_a) - B] / V$$

Where:

V_s = original sample volume (step 8; normally 50 mL)
 V_a = aliquot volume (step 9; normally 20 mL)
 B = average amount of mercury present in the media blanks

EVALUATION OF METHOD:

Rathje and Marcero originally used Hopcalite (MSA, Inc.) as the sorbent material [8]. Later, Hopcalite was shown superior to other methods for the determination of mercury vapor [9]. Atmospheres of mercury vapor for the study were dynamically generated in the range 0.05 to 0.2 mg/m^3 and an adsorbent tube loading of 1 to 7 μg was used. The Hydrar material used in the present method is similar to Hopcalite. No significant difference in the laboratory analysis of mercury collected on the two sorbent materials was observed [10]. OSHA also validated a method for mercury using Hydrar [3]. An average 99% recovery, with $s_p = 0.042$, was seen for 18 samples with known amounts (0.9 to 3 μg) of mercury added (as $\text{Hg}(\text{NO}_3)_2$) [11]. No change in recovery was seen for samples stored up to 3 weeks at room temperature or up to 3 months at -15°C ; longer storage times were not investigated [11].

REFERENCES:

- [1] NIOSH Testimony, OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.



U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOP: 1827
PAGE: 19 of 19
REV: 2.0
DATE: 05/13/99

ANALYSIS OF MERCURY IN AIR WITH A MODIFIED NIOSH 6009 METHOD

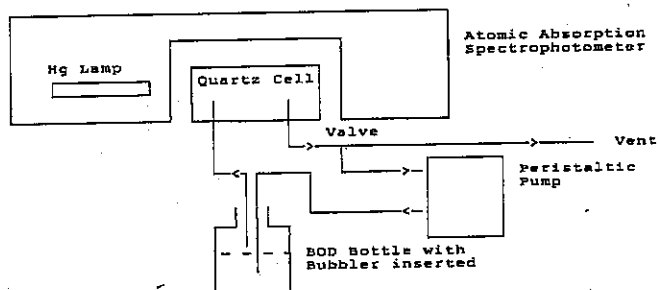
MERCURY

METHOD: 6009

- [2] Evaluation of Mercury Solid Sorbent Passive Dosimeter, Backup Data Report, Inorganic Section, OSHA Analytical Laboratory, Salt Lake City, Utah, 1985.
- [3] Mercury in Workplace Atmospheres (Hydrar Tubes), Method ID 145H, Inorganic Section, OSHA Analytical Laboratory, Salt Lake City, Utah, 1987.
- [4] NIOSH/MRSB. Reports for Analytical Sequence Nos. 5854, 5900, 6219, and 6311, NIOSH (Unpublished, 1987-1988).
- [5] NIOSH Manual of Analytical Methods, 3rd. ed., Method 6000. (1984).
- [6] NIOSH Manual of Analytical Methods, 2nd. ed., V.4, 5199, U.S. Dept. of Health, Education, and Welfare Publ. (NIOSH) 78-175 (1978).
- [7] Ibid., V.5, P&CAM 175, Publ. (NIOSH) 79-141 (1979).
- [8] Rathje, A. O., Marcero, D. H. Improved hopcalite procedure for the determination of mercury in air by flameless atomic absorption, Am. Ind. Hyg. Assoc. J. 37:311-314 (1976).
- [9] McCammon, C. S., Edwards, S. L., Hull, R. D., Woodfin, W. J., A comparison of four personal sampling methods for the determination of mercury vapor, Am. Ind. Hyg. Assoc. J., 41:528-531 (1980).
- [10] Internal Methods Development Research, Data Chem, Inc., Salt Lake City, Utah (1982).
- [11] Eller, P.M., NIOSH, unpublished data (1987-88).

METHOD WRITTEN BY: Keith R. Nicholson and Michael R. Steele, Data Chem, Inc., Salt Lake City, Utah, under NIOSH contract No. 200-87-2533.

APPENDIX: Cold Vapor Mercury Analysis System



1. The valve should direct the vented vapors to a hood or to a mercury scrubber system.
2. When the valve is opened to "Vent" the peristaltic pump should draw room air. Place a Hydrar tube in the air intake to eliminate any mercury that may be present.
3. Adjust the peristaltic pump to a flow which will create a steady stream of bubbles in the BOD bottle, but not so great that solution droplets enter the tubing to the quartz cell.
4. If water vapor condenses in the quartz cell, heat the cell slightly above room temperature by wrapping it with a heating coil and attaching a variable transformer.
5. The bubbler consists of a glass tube with a bulb at the bottom, slightly above the bottom of the BOD bottle. The bulb contains several perforations to allow air to escape into the solution (in a stream of small bubbles). A second tube is provided to allow the exit of the vapor. The open end of the second tube is well above the surface of the liquid in the bottle. The two tubes are fixed into a stoppering device (preferably ground glass) which fits into the top of the bottle. A coarse glass frit can be used in place of the bulb on the first tube. However, it is more difficult to prevent contamination when a frit is used.
6. Replace the flexible tubing (Tygon or equivalent) used to connect the bubbler, cell, and pump periodically to prevent contamination due to adsorption of mercury.

APPENDIX F

Mercury Screening Form

Site Name: _____ TDD #: _____

Date of Screening: _____ Time initiated: _____

Name of Contact: _____ Phone: _____

Address: _____

Type of structure (circle one): Residential, commercial, school, other (specify)_____

Number of occupants: _____ Ages (if a residence): _____

Suspected date of spill: _____

Current outdoor ambient temperature: _____

Status of ventilation (check one): _____ 1. Outside windows/doors open.
 _____ 2. Windows closed, interior doors open.
 _____ 3. Door and windows to spill area closed.

Was there any attempt to clean spill? Y N

Any mercury-related illnesses reported? Y N

Screening: Instrument (check): Jerome_____ Lumex_____

Write peak reading for each room listed below. Specify units.

Room Type: _____ Specific Location: _____

Floors: _____

Breathing Zone: _____

Vents: _____

Other:

Figure 1 consists of two line graphs. The left graph is for the 'same' condition, and the right graph is for the 'different' condition. Both graphs plot the percentage of correct responses (Y-axis, 0 to 100) against age in years (X-axis, 5 to 9). The 'same' condition shows a positive linear trend, starting at approximately 65% for 5-year-olds and reaching about 85% for 9-year-olds. The 'different' condition shows a negative linear trend, starting at approximately 65% for 5-year-olds and decreasing to about 45% for 9-year-olds. Error bars representing standard error are shown for each data point.

Figure 1 consists of a 3x3 grid of scatter plots. The rows are labeled 'Single parent', 'Two parent', and 'Three parent' on the left. The columns are labeled 'Single parent', 'Two parent', and 'Three parent' on top. Each plot has 'Number of children in the household' on the x-axis and 'Number of children in the family' on the y-axis. The data points are represented by small circles. In the 'Single parent' row, the plots show a clear positive linear relationship. In the 'Two parent' and 'Three parent' rows, the relationships are more scattered, with some points showing a positive relationship and others showing a negative or no relationship.

[illegible]

**Residential Mercury Contamination
Screening Checklist**
(to be used when residence is known to be contaminated)

(√) or (N/A)

Vacuum cleaner (bag)		Car (both sides floor and seat in front and back)	
Furnace filter		Tool boxes	
Heating ducts		Baseboard areas	
Clothing (bag and screen)		Tile crevices	
Shoes (especially tongue areas)		Cracks in floor	
Clothes hamper		Concrete floors	
Bedding (between sheets, especially at level of feet)		Near bottom of brick wall	
Clothes washer (inside)		Lower shelving and items on shelf	
Clothes dryer (inside and lint trap)		Dusty areas	
Heavy traffic areas of floor		Under edge of linoleum or vinyl tile	
Heavy traffic areas of carpet (especially near bed, TV viewing area)		Crevices of hardwood flooring	
Sink drains		Above drop ceiling tiles (especially if spill occurred on floor above)	
Jewelry (bag and screen)		All garage areas	
Porous items (books, wooden objects, etc.)		Throw rugs	
Coins (bag and screen)		Welcome mats	
Food-related items in contaminated areas (bag and screen)		Furniture	
Electronics		Under major appliances	

APPENDIX G

USEPA Access Agreement



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 9
EMERGENCY RESPONSE BRANCH
75 Hawthorne Street
San Francisco, California 94105

CONSENT FOR ENTRY AND ACCESS TO PROPERTY

Name: _____

Address: _____

Phone: _____

Address of Property for which consent to access is granted:

Relationship to property: _____
(i.e., owner, 5-year tenant, etc.)

I consent to officers, employees, and authorized representatives of the United States Environmental Protection Agency (USEPA) entering and having continued access to my property for the following purposes:

1. Air and wipe sampling;
2. Decontamination of structures, fixtures and furnishings contaminated by mercury;
3. Stabilization and disposal of contaminated structures, furnishings, and/or fixtures which remain contaminated, including in some cases, the removal of contaminated building components such as carpets, floors, walls, ceilings and paneling;
4. Installation of carpet, floors, and walls (if necessary due to #3 above);
5. Removal of contaminated soil, if necessary; and
6. Such other actions as the USEPA On-Scene Coordinator determines necessary to protect human health, welfare, or the environment.

I realize that these actions by the USEPA are undertaken pursuant to its response authorities under the Comprehensive Environmental Response, Compensation and Liability Act of 1980, as amended (CERCLA), 42 U.S.C. § 9601 et seq.

I also realize that there may be a loss of or damage to of property during these actions. I addition, I realize USEPA will be utilizing my utilities, including heat, water, and electricity.

To the extent that USEPA does replace any item determined to be contaminated, I acknowledge that it makes no representations about the quality, aesthetics, safety, use or character of such item or its installation. Furthermore, USEPA makes no warranties as to such item or its installation, including but not limited to warranties of merchantability or fitness for purpose.

I also consent to local and state health officials reviewing this work, not otherwise covered by this agreement, entering and having access for the property, if any, due to the activities performed pursuant to this agreement.

This written permission is given by me voluntarily with knowledge of my right to refuse and without threats or promises of any kind.

I certify that this Consent for Entry and Access is entered into voluntarily and constitutes an unconditional consent and grant of permission for access to the property by officers, employees, and authorized representatives of USEPA for the purposes specified above at all reasonable times.

Date

Signature

APPENDIX H

Amalgamation Process

-Amalgamation-

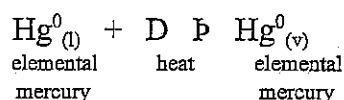
Oxidation States	Elemental(Hg^0), Mercuric(Hg^{+2}), Mercurous(Hg_2^{+2}), Sulfide(S^{-2})
Density_(Hg)	13.546g/cm ³
Density_(S)	2.07g/cm ³
Molecular Weight_(Hg)	200.59 ^g /mole
Molecular Weight_(S)	32.066 ^g /mole
Vapor Pressure_(Hg)	0.0012mmHg at 20°C (68°F)
Vaporization Rate_(Hg)	0.007mg/cm ² •hr for 10.5cm ² droplet at 20°C

Amalgamation:

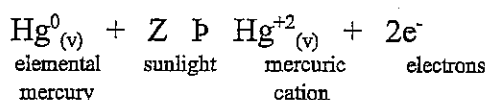
Amalgamation of elemental mercury is a physical immobilization process that incorporates mercury with inorganic reagents such as copper, gold, nickel, zinc or sulfur to form a semisolid substance.¹ Elemental mercury dissolves in the inorganic reagent, forming a solid solution that lowers the vapor pressure of elemental mercury, ultimately lowering the amount of mercury vapors released into the air.

Amalgamation with a metal, such as copper, gold, nickel and zinc, does not involve a chemical reaction, but rather electrostatic forces. Amalgamation with a nonmetal, such as sulfur, does involve a chemical reaction. The following set of equations describe the amalgam process with sulfur.

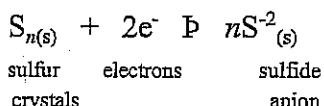
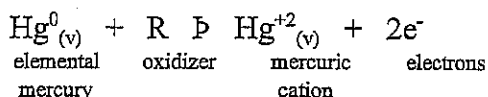
1) Vaporization Reaction:



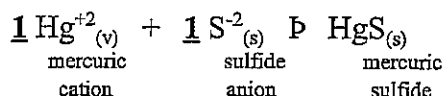
2) Redox Reactions:



and/or



3) Amalgamation Reaction:



Sulfur Application:

The 1:1 ratio of mercury to sulfur used in the amalgamation reaction can be used to determine the amount of sulfur needed to clean-up the spilled mercury. Since densities differ between the two substances, a weight or volume ratio of mercury to sulfur can be used. The following calculations display the weight and volume ratios of mercury to sulfur necessary for the clean-up processes of mercury.

**Stoichiometry
Calculations:**

<u>Weight</u>	or	<u>Volume</u>
1 mole _[Hg] H 200.59 ^g / _{mole} = 200.59g		200.59g) 13.546 ^g / _{cm³} _[Hg] = 14.81cm ³
1 mole _[S] H 32.066 ^g / _{mole} = 32.066g		32.066g) 2.07 ^g / _{cm³} _[S] = 15.49cm ³
_[Hg] / _[S] : 200.59g) 32.066g = 6.26		_[Hg] / _[S] : 14.808cm ³) 15.49cm ³ = 0.96

The amount of sulfur needed to clean-up the spilled mercury can be determined by dividing the weight or volume amounts of mercury by the corresponding ratio factors. The result will be the approximate amount of sulfur needed to amalgamate mercury.

For example: 50lbs. _[Hg]) **6.26** . 8lbs. _[S] or 50gal. _[Hg]) **0.96** . 48gal. _[S]

*Note: These calculations are meant for pure elemental mercury only. For mixed waste streams containing mercury, an educated guess using the above information is best at hand.

Other Information:

- The oxidation of elemental mercury to the mercuric ion is the rate limiting step in the amalgam process. The increase of mercuric ions produced through the oxidation of elemental mercury will accelerate the amalgam reaction. This is achieved through sunlight exposure and through the addition of oxidizing agents.
- The relocation of mercury is an issue of concern created during a mercury response. Mercury vapors will travel through the air and condense back to elemental form when conditions are ideal. Thus, sufficient sulfur application must occur immediately to prevent any movement of mercury vapors.
- The problematic situation dealing with mercury is where a porous and large surface area of contamination exists, ie. asphalt. Difficult conditions such as these could possibly call for total removal of contaminated areas. "Mercury may be chemically bound to a matrix constituent or trapped in the matrix. Thus, it is more practical to stabilize the contaminated material rather than extracting only the mercury."²

¹. Code of Federal Regulations, Title 40, Part 268, Section 268.42

². Ebadian, M.A., Marshall Allen, Yong Cai, Mercury Contaminated Material Decontamination Methods: Investigation and Assessment, Florida: FIU, 2001.

APPENDIX I

Contaminated Items Documentation Log

APPENDIX J

Quick Reference Sheets for Operating Lumex and Jerome

Lumex[®] Mercury Analyzer

EPA Equipment # 28 and # 28a
Model RA915+
January 2003

NOTE: Calibration/use of this instrument should be recorded in the log book.

Quick Start-up and Operation:

NOTE: Remove the unit from the cloth case to access the test toggle switch.



1. Attach hose by inserting then turning the connection clockwise. Make sure it is snug. Make sure dust filter is present.
2. Turn “POWER” switch on (red rocker switch on front end). LCD display will show Lumex Title Screen.
3. Let unit warm up for 15 minutes.

NOTE: Complete Test Run (nos. 4 to 9) below prior to use

4. Press “ENT” button on top until LCD display will show “*Main Menu.”
5. Press black push button labeled “Lamp Ignition” that is next to power switch. The “*” will disappear. Let the lamp warm up for five minutes.
6. Arrow down to Test and press “ENT” button.
7. After warmup, message will read “Enter the Test Cell.” Toggle the test cell switch located on the side of the instrument between on and off several times. **Leave the switch in the “ON” position.**
8. Press “ENT.” You will see a reading by the R(%) (relative standard deviation). If the R equals <25%, it is ready to use.
9. Press “ESC.” The “Remove the Test Cell” message will appear. **Toggle test switch to off.**

NOTE: To conduct monitoring, follow procedures below. The instrument is sensitive to temperature changes and takes some time to stabilize.

10. Press “ENT” to get back to Main Menu screen.
11. Arrow down to **On Stream.**

12. Press “ENT” button. Baseline test runs for 20 seconds. Readings then begin (expressed as nanograms per cubic meter), with update every second in the upper right corner of LCD screen (as shown below).

Sm ng/m³

S:

Si:

10 *

Notes:

S Current value

Si Current mean value

Sm Name of measurement mode, i.e., ON STREAM

* Frame time, i.e, 10-second countdown

13. Press “ENT” again. Readings continue every second, but with various summary functions.

- Three 10-second averages are displayed after 1: 2: and 3:
- After 30 seconds, a 30-second average will be displayed after “Sc:”
- Below “Sc:” the associated Relative Standard Deviation will be displayed after “R(%)” (as shown below). Instantaneous values are displayed after “S:,” while the running mean is displayed after “Si:”

Sm	ng/m ³
1:	S: 213
2:	
3:	Si: 209
Sc:	
R (%) =	10
*	

Notes:

S Current value

Sc 30-second mean

Si Current mean value

Sm Name of measurement mode, i.e., ON STREAM

1-3 10-second mean values

* Frame time, i.e, 10-second countdown

14. At this point, there are three choices:

- Calculate another 30-second average by pressing “ENT” again (can be done many times).
- Turn off machine: Press “ESC”, and then turn the red Power switch to “OFF.”
- Calculate a new baseline (especially if you are trying to measure very subtle effects and want to be sure of your zero): press “ESC”, down arrow to “On stream”, then press “ENT” (You are back to step 12).

NOTE:

1. Deviation (R%) value disappears if the 30-second mean (Sc) is smaller than the preset detection limit.
2. During ON STREAM measuring, the compressor can be switched off by pressing the down arrow, thus saving battery life during pauses in sampling.
3. The ALARM warning may appear during operation in Sm mode. This means that mercury vapor concentrations exceed the preset HIGH limit.

Calibration/Operational Test:

The RA-915+ Mercury Analyzer performs an internal calibration check every time it is turned on. When the calibration cell shows a relative standard deviation (R) of greater than 25%, it should be sent to the manufacturer for recalibration/service.

Additional Operation Information:

- The detection range of the Lumex is 2 nanograms per cubic meter (ng/m³) to 26 micrograms per cubic meter (Fg/m³) in air.
- The Lumex also has a 3.02 series software that goes with the mercury analyzer. The RA915 software allows the user to process, store, and visualize data obtained from the analyzer (consult the software manual).
- The RA915 analyzer can be used with the display unit or with a stand-alone PC. Refer to the operation and software manual for specific information.

Mercury Health Effects:

The nervous system is very sensitive to all forms of mercury. Exposure to high levels of mercury can permanently damage the brain and kidneys. Short-term exposure to high levels of metallic mercury vapors may also cause lung damage, nausea, vomiting, diarrhea, increased blood pressure and heart rate, skin rashes, and eye irritation. Very young children are more sensitive to mercury than adults. Mercury can pass to an unborn fetus and also to a nursing infant.

NOTE: If Level C PPE is required for monitoring activities, mercury-specific APR cartridges are needed. The person recovering visible mercury must don a respirator.

Action Levels:

NOTE: These action levels are designed for human breathing zones.

DESCRIPTION	ng/m ³ (10 ⁻⁹)	Fg/m ³ (10 ⁻⁶)	mg/m ³ (10 ⁻³)
IDLH	10,000,000	10,000	10.0
NIOSH REL	50,000	50.0	0.05
OSHA PEL (ceiling)	100,000	100	0.10
ACGIH TLV	25,000	25.0	0.025
USEPA Residential Cleanup Goal	300	0.30	0.0003
USEPA Non-Residential Cleanup Goal (TWA)	1,300	1.30	0.0013

Note:

ng/m³ Nanograms per cubic meter

Fg/m³ Micrograms per cubic meter

mg/m³ Milligrams per cubic meter

ACGIH TLV American Conference of Governmental Industrial Hygienists Threshold Limit Value

IDLH Immediately Dangerous to Life and Health

NIOSH REL National Institute for Occupational Safety and Health Relative Exposure Limit

OSHA PEL Occupational Safety and Health Association Permissible Exposure Limit

TWA Time Weighted Average

Detection Limits (Lumex vs. Jerome):

Mercury Vapor Analyzers	ng/m ³ (10 ⁻⁹)	Fg/m ³ (10 ⁻⁶)	mg/m ³ (10 ⁻³)
Lumex	2.00	0.002	0.000002
Jerome	3,000	3.00	0.003

Note: 1 ng/m³ = 0.001 Fg/m³ = 0.000001 mg/m³

1 mg/m³ = 1,000 Fg/m³ = 1,000,000 ng/m³

Routine Maintenance:

Maintenance Needed	Frequency	Performed By	Manual Reference
Change Dust Filter	On a regular basis, or when visual dust particles are noted on the filter.	WOS CONTRACTOR	Pages 25 to 28
Change Absorption Filter	On a regular basis, or when visual particles are noted on the filter.	WOS CONTRACTOR	Page 26
Factory service/recalibration	When R is >25%, or as needed	Ohio Lumex Co.	Pages 17 to 18, 21

Note: R = Relative deviation of the three measured mercury vapor concentrations from the averaged calibration cell value (in percent)

Change the dust filter on a routine basis. As soon as you see visible discoloration on the intake, it needs changing. When changing the dust filter, the device should be switched off. The absorption filter is located in Inlet 1 at the front panel of the analyzer. To remove the filter from the analyzer, grip it with tweezers and pull it out. Insert a new filter into Inlet 1, exercising caution not to push through the screen on the valve. Refer to manual for additional instructions regarding the changing of absorption and dust filters.

Principles of Operation:

The Lumex is based on differential Zeeman atomic absorption spectrometry using high frequency modulation of light polarization. A radiation source is placed in a permanent magnetic field. The mercury resonance line is split into three polarized Zeeman components. When radiation propagates along the direction of the magnetic field, a photodetector detects only the radiation of mercury components. When mercury vapor is absent in the analytical cell, the radiation intensities of both components are equal. When absorbing atoms appear in the cell, the difference between the intensities of the components increase as the mercury vapor concentration grows.

Applications:

- Portable atomic absorption spectrometer designed to determine the mercury content in ambient air, water, soil, and natural and stack gases.
- The analyzer can be used for measuring mercury vapor concentrations in the air, both in a stationary mode and in continuous mode from vehicles.
- Data collection and data logging are conducted in real-time.
- The sampling rate is set at 20 liters per minute.
- The instrument has a built in calibration cell and performance check cell.
- It has a built in compressor and internal rechargeable power source, as well as a car adapter, for field monitoring in remote areas.
- Able to achieve detection limits below residential action levels

Limitations:

- Temperature-sensitive; needs time to stabilize.
- Dusty environments and moisture (high humidity) have been shown to absorb mercury during sample collection, giving inaccurate results.
- The Lumex is a fragile instrument; strong vibrations and shocks while in use and transit may result in inaccurate readings.
- This instrument is not intrinsically safe.

Battery Charging Schedule:

- The battery charger should remain attached to the instrument until it is ready for use in the field.
- Leave unit off while charging; green charge light only comes on if the battery is completely discharged.
- Do not store the unit with a discharged battery for more than three days to avoid permanent damage.
- It takes approximately 5 hours to charge a dead battery.
- A fully charged battery provides continuous operation of the analyzer for approximately 3 ½ hours.
- When the unit is being operated, the red discharge light will come on indicating that the battery is discharging.

Main Inventory of Items/Accessories:

- Base Unit
- Display and control unit
- Power supply unit
- Operation manual
- Kit of spare parts and accessories
- Canvas Shoulder bag
- Display-unit-connection cable
- Air intake hose with pre-filter
- Analyzer-PC interface cable (RS-232 standard)
- Software for RA-915+ (4 disks)

Replacement of Auxiliary Equipment/Supplies:

Replacement of auxiliary equipment is dependent on the frequency of use, as indicated in the previous maintenance schedule. Loaner units are available from Ohio Lumex Company on a 24-hour basis.

Contact Information (Technical Support):

<http://www.ohiolumex.com/>

Ohio Lumex Company

9263 Ravenna Rd., Unit A-3

Twinsburg, Ohio 44087

Telephone: (888) 876-2611

and (330) 405-0837

Fax: (330) 405-0847

email: mail@ohiolumex.com

Instrument Panel:



Database Parts List

Part Number	PartType	Other Part Name	Part Description
28-1166		Air Intake Hose with pre-filter	
28-476		Display and Control Unit	
28-470		Display Unit Connection Cable	
28-472		RS-232 Connector Cable	
28-473		Software—4 disks	
28-1825	Tweezers	For Dust filter—straight & pointed	
28-474	Battery	Internal	
28-475	Battery Charger		
28-825	Case		
28-469	Case	Canvas Shoulder Bag	
28-1126	Filter	1 1/2 inch Filter (Round, Flat)	Unknown use
28-467	Filter	SRK Absorption Filter	Zero Mercury Absorption filter—see p 26 of manual
28-1125	Filter	SRK Antidust Filter	Dust Filter—see p 26 of manual
28-468		Instruction Manual	
28-893		Instruction Manual	For software
28-658		Instruction Manual	Quick Start Guide

Jerome 431-X Mercury Vapor Analyzer Cheat Sheet

1. Press the **ON** button. Display should read .000. A **LO BATT** message appears briefly in upper left corner. If **LO BATT** light persists, battery must be charged. Allow instrument to warm up for approximately 1 minute.

2. Check voltage setting(110 or 220 VAC) on the back of the instrument. If voltage must be changed, turn knob. (To change frequency setting, see pg. 16 of manual.)



3. Perform a sensor regeneration:

- Plug the line cord into the instrument using the plug in the back and to an AC power outlet.
- Power the instrument **ON** and press the **REGEN** button. The instrument will begin a 10 minute regeneration cycle, indicated by **.H.H.H** flashing on the display. **Do not interrupt this cycle.** If any error message, such as **.H.L.P.** or **.L.L.L.**, appears, see pg. 19 of manual.
- Adjust the sensor zero by pressing the **ZERO** button and turning the zero adjust screw located under the handle. Adjust until display reads 0.
- **Note:** A minimum 30 minute wait after the sensor regeneration is complete, ensures maximum sample accuracy. However, the unit can be used immediately following the sensor regeneration if necessary.

4. The instrument is now ready to sample. Note that as the instrument measures mercury, the **ZERO** will display **H**. **Do not adjust the ZERO after instrument has measured mercury and before the next regeneration.** (Occasionally the **ZERO** may drop to **L** (for low) between the initial zeroing and the first sample. It is OK to readjust the **ZERO** if the instrument has not measured mercury).

5. Press the **SAMPLE** button to start a 10 second sampling cycle. **Do not allow the probe or the instrument's intake to come into contact with liquids. The instrument is not intrinsically safe.** At the end of the 12 second cycle, read the digital meter.

- **Note:** If the sensor becomes completely saturated, the digital meter displays **.8.8.8** instead of a value. A sensor regeneration must then be performed.
- The probe may be plugged directly into the instrument's intake to locate mercury vapor in hard to reach places.

6. At the end of the day, perform a sensor regeneration again. When complete, store the instrument with the zero air filter in the intake.

Survey Mode- instrument takes samples every 3 seconds automatically

To activate Survey Mode:

- Press the **ON** button. Allow unit to warm up for approximately 1 minute.
- Press and **hold** the **SAMPLE** button. The instrument takes a normal 12 second sample, displays concentration at end of cycle, and then goes into **survey mode** sampling every 3 seconds.
- When finished surveying, **release** the **SAMPLE** button.

To lock instrument in Survey Mode:

- Follow the above first 2 steps.
- Hold down the **SAMPLE** button until sensor status indicator bars(s) “__” begins flashing on the display. Press the **ZERO** button, then release the **SAMPLE** button. The pump should continue to run and display should update every 3 seconds
- The instrument remains in survey mode until one of the following occurs:
 - sensor is saturated
 - a LO BAT signal appears
 - a HL (high level mercury level) is encountered
 - instrument is turned OFF