

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

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 $\leq 10 \mu\text{g}/\text{m}^3$; 100 observations
- Lumex vs. NIOSH; NIOSH $\leq 1 \mu\text{g}/\text{m}^3$; 62 observations
- Tracker vs. NIOSH; 156 observations
- Tracker vs. NIOSH; NIOSH $\leq 10 \mu\text{g}/\text{m}^3$; 125 observations
- Tracker vs. NIOSH; NIOSH $\leq 1 \mu\text{g}/\text{m}^3$; 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 ≤ 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 ≤ 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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8 References

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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 \leq 10		Lumex vs. NIOSH; NIOSH \leq 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 \leq 10		Tracker vs. NIOSH; NIOSH \leq 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 \leq 1	Lumex#2 All Data	Lumex#2 NIOSH \leq 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 \leq 1	Tracker#2 All Data	Tracker#2 NIOSH \leq 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

Lumex RA915+ Data

106 Observations

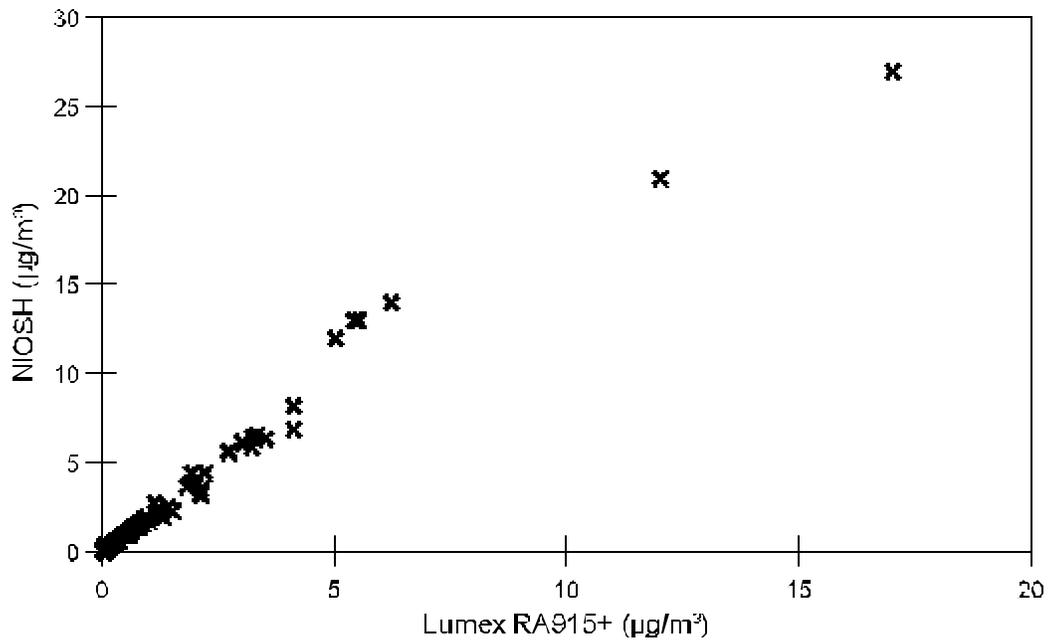


Figure 1. Laboratory (NIOSH 6009) and Field (Lumex RA915+) Mercury Results

Tracker 3000 Data

156 Observations

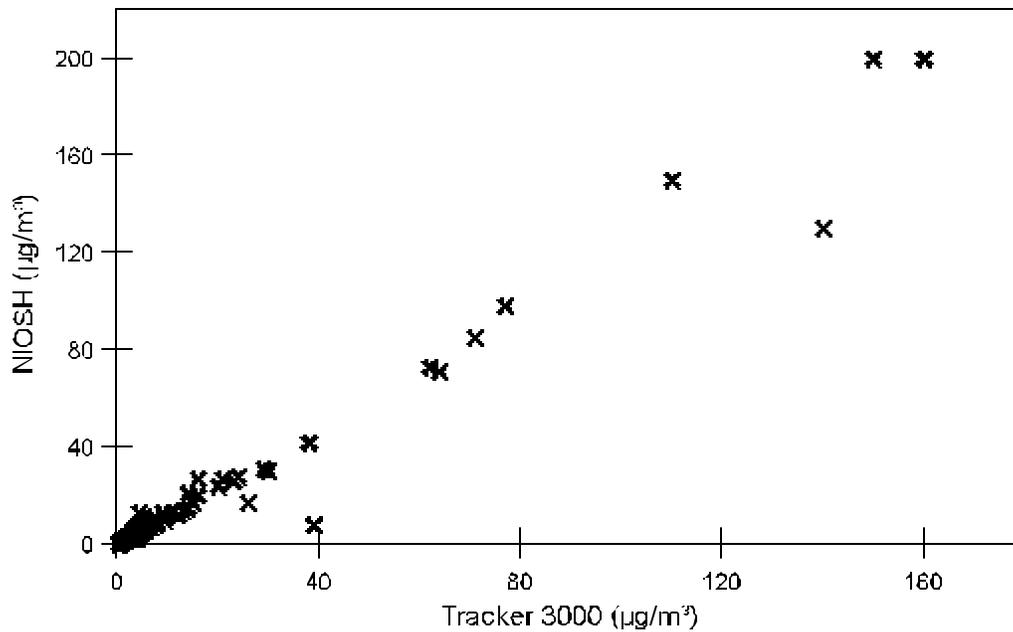


Figure 2. Laboratory (NIOSH) and Tracker 3000 Mercury Results

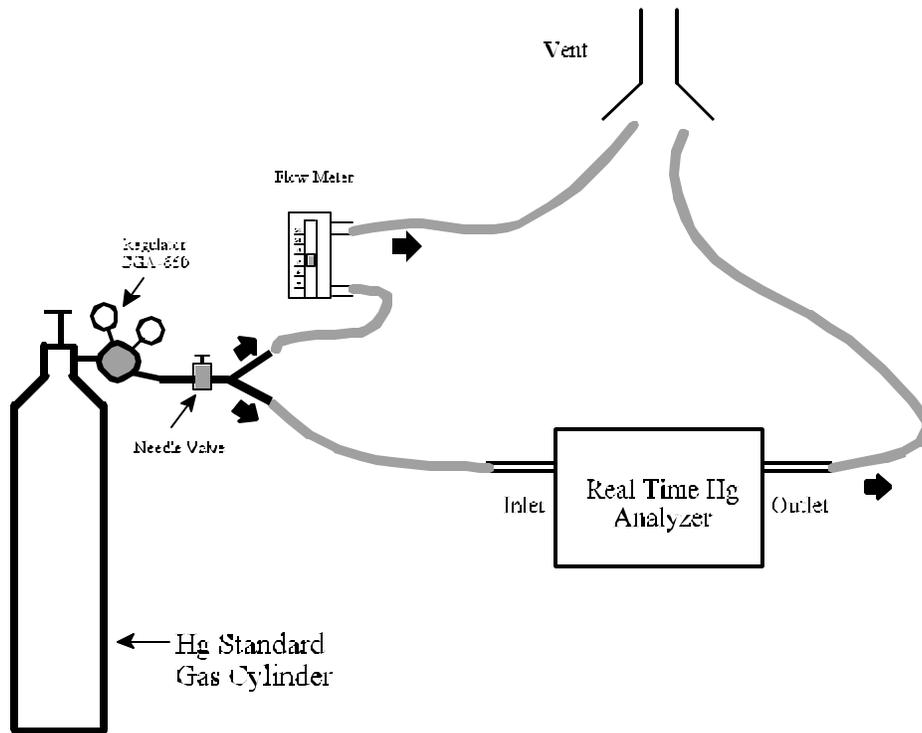


Figure 3. Setup for Calibrating Real-Time Mercury Analyzers

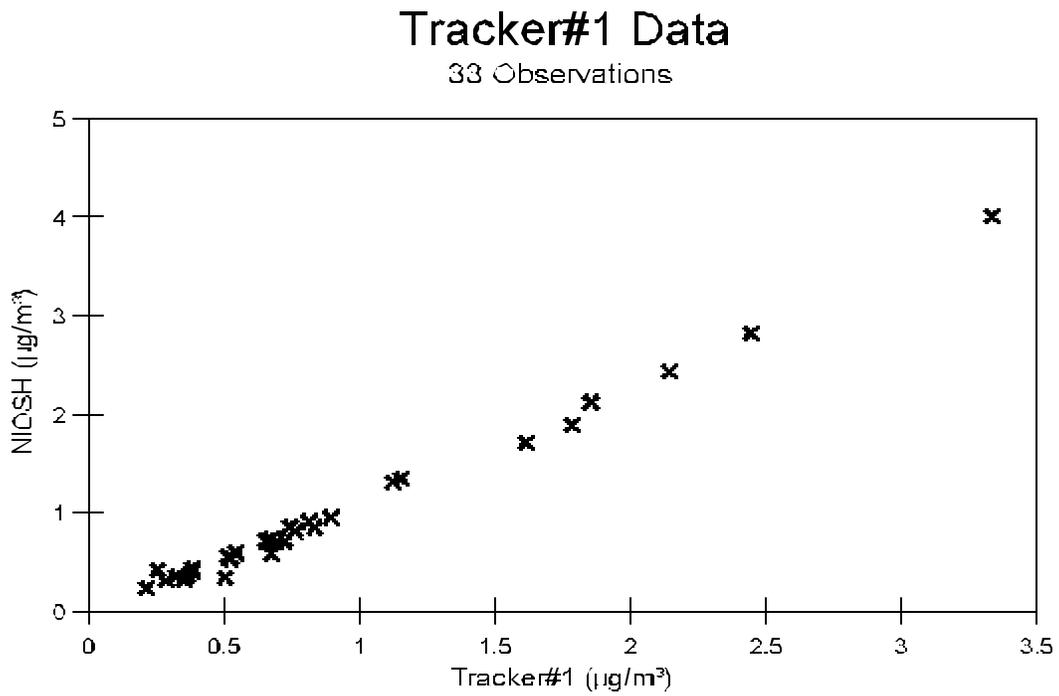


Figure 4. Laboratory and Tracker#1 (Calibrated) Mercury Results

Tracker#2 Data

33 Observations

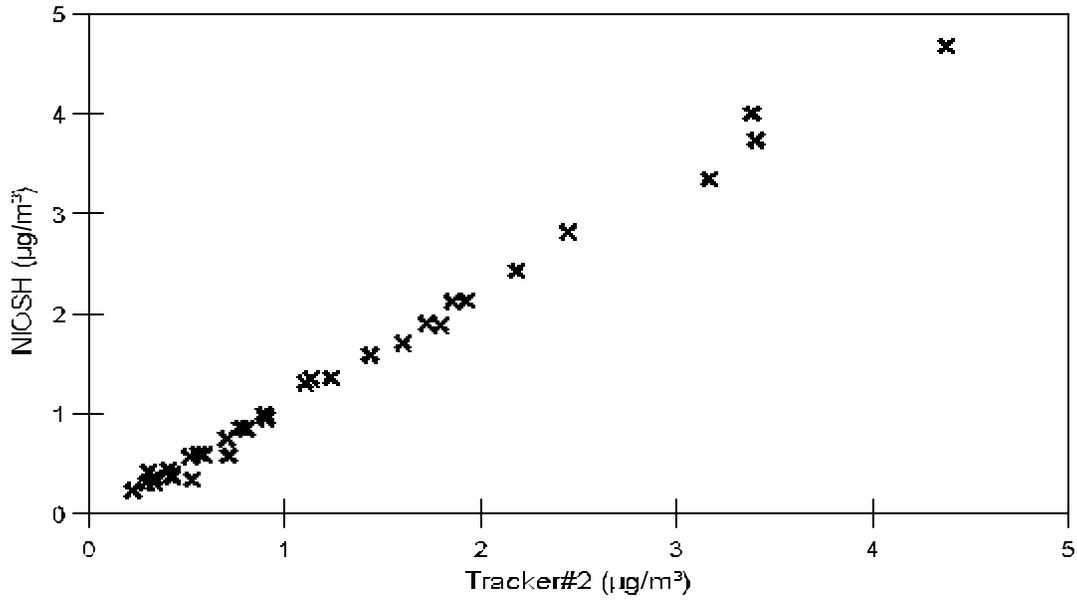


Figure 5. Laboratory and Tracker#2 (Calibrated) Mercury Results

Lumex#1 Data

15 Observations

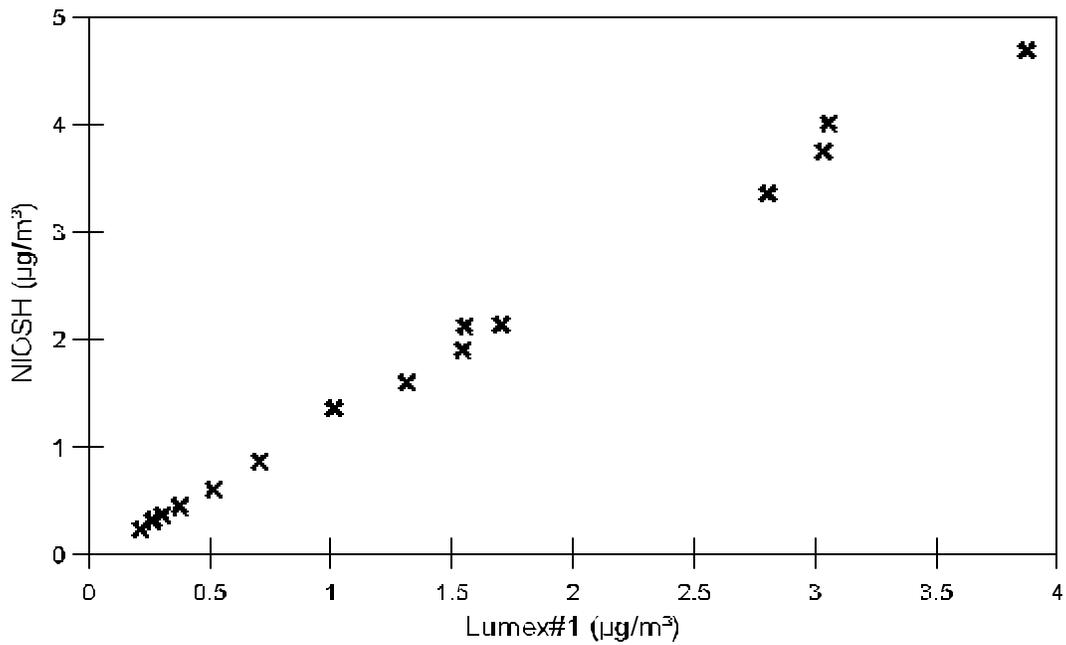


Figure 6. Laboratory and Lumex#1 (Calibrated) Mercury Results

Lumex#2 Data

10 Observations

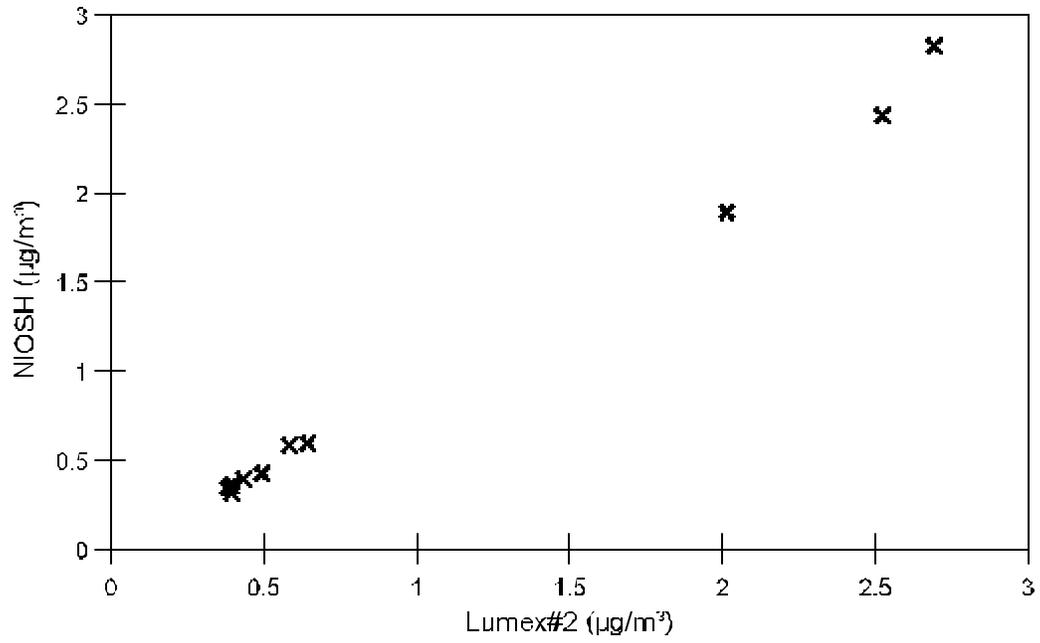


Figure 7. Laboratory and Lumex#2 (Calibrated) Mercury Results

