ANALYTICAL METHOD FOR INDOOR AIR MONITORING OF METALLIC MERCURY VAPORS

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ABSTRACT

Metallic mercury vapor levels were monitored inside 50 homes to evaluate spill site cleanup operations. National Institute for Occupational Safety and Health (NIOSH) Method 6009, Mercury, was modified to measure levels of mercury as low as 0.05 micrograms per cubic meter ($\mu g/m^3$) for a 200-liter (L) air sample. This modification enables the response team to meet the action level (0.3 $\mu g/m^3$) for indoor air set by the Agency for Toxic Substances and Disease Registry (ATSDR). Measurements taken in the field using a Jerome 431™ Mercury Vapor Analyzer were compared with laboratory measurements using the modified NIOSH Method 6009. Mercury concentrations measured using the Jerome 431 instrument could not be correlated statistically with concentrations measured in the laboratory for this study.

INTRODUCTION

In August 1994, children discovered four 250-milliliter (mL) containers of metallic mercury in an abandoned van in Belle Glade, Florida (Figure 1). The children began sharing the mercury with their friends, spreading it throughout the neighborhood and local high school.

Figure 1. Abandoned Van Identified as Source of Mercury

The United States Environmental Protection Agency (U.S. EPA) Region IV responded to assess the mercury contamination and provide assistance to the Florida Department of Environmental Protection (FDEP) and local authorities. Later, the U.S. EPA Region IV requested the assistance of the U.S. EPA/Environmental Response Team (ERT) to respond to the mercury spill and to provide technical support in order to assess the threat to human health and the environment resulting from the mercury spill.

A Jerome Mercury Vapor Analyzer was used for assessing the initial extent of metallic mercury vapor contamination at the spill site. However, the standard set by ATSDR for long-term residential exposure to mercury was below the level detectable by Jerome analyzer being used. NIOSH Method 6009 was modified to incorporate more concentrated sample solutions than was typical for the standard method. This allowed detection of metallic mercury vapor levels well below the maximum allowable level set by ATSDR.

SAMPLING AND DECONTAMINATION METHODS

The suspected contaminated areas were screened with a Jerome 431™ Gold Film Mercury Vapor Analyzer. The response team assigned a cleanup priority based on these results and mercury "hot spots" were identified within each structure. Decontamination procedures were implemented, and the houses were tested again. Once the mercury concentrations fell below the Jerome detection limit, clearance sampling was performed using modified NIOSH method 6009 to ensure that the long-term exposure level was not exceeded. All preliminary air sampling was performed under normal living conditions. Within the school, samples were collected in the center of each room.

A specially equipped vacuum cleaner was used to remove the metallic mercury from the contaminated carpets, furniture, and personal effects in the affected houses and school areas. Floor areas where mercury had been observed were treated with HgX™ or Mercosorb™. Remaining hot spots were cleaned with Merconwipes™, and air purifiers were run in some locations.

LABORATORY ANALYSIS METHOD

Indoor metallic mercury vapors were sampled following a modified NIOSH Method 6009 [(1)]. These vapors were collected on 200-milligram (mg) Hopcalite™ tubes in the homes using personal sampling pumps. The nominal flow rate was programmed to 0.75 liters per minute (L/min) with a sampling time of 270 minutes. Sampling stations were set up in the living room and bedrooms of each residence.

The sorbent material from each tube was quantitatively transferred to a 100-mL Class A volumetric flask, and digested by adding 2.5 mL of nitric acid followed by 2.5 mL of concentrated hydrochloric acid. After digestion, the sample was diluted to the 100-mL volume with distilled water. The resulting solution is more concentrated than that used with NIOSH Method 6009, thus allowing a detection limit of 0.05 $\mu g/m^3$, well below the limit accessible using the original NIOSH method.

The digested sample was analyzed using cold vapor atomic absorption (AA) spectroscopy with no further dilution. The AA calibration range was 0.2 to 5.0 micrograms per liter (μg/L) with a detection limit of 0.1 μg/L (0.05 $\mu g/m^3$ for a 200-L air sample). The method working range was 0.1 to 2.5 $\mu g/m^3$ for a 200-L air sample. Selected duplicate samples were sent to a commercial and Florida Department of Health laboratories for verification.

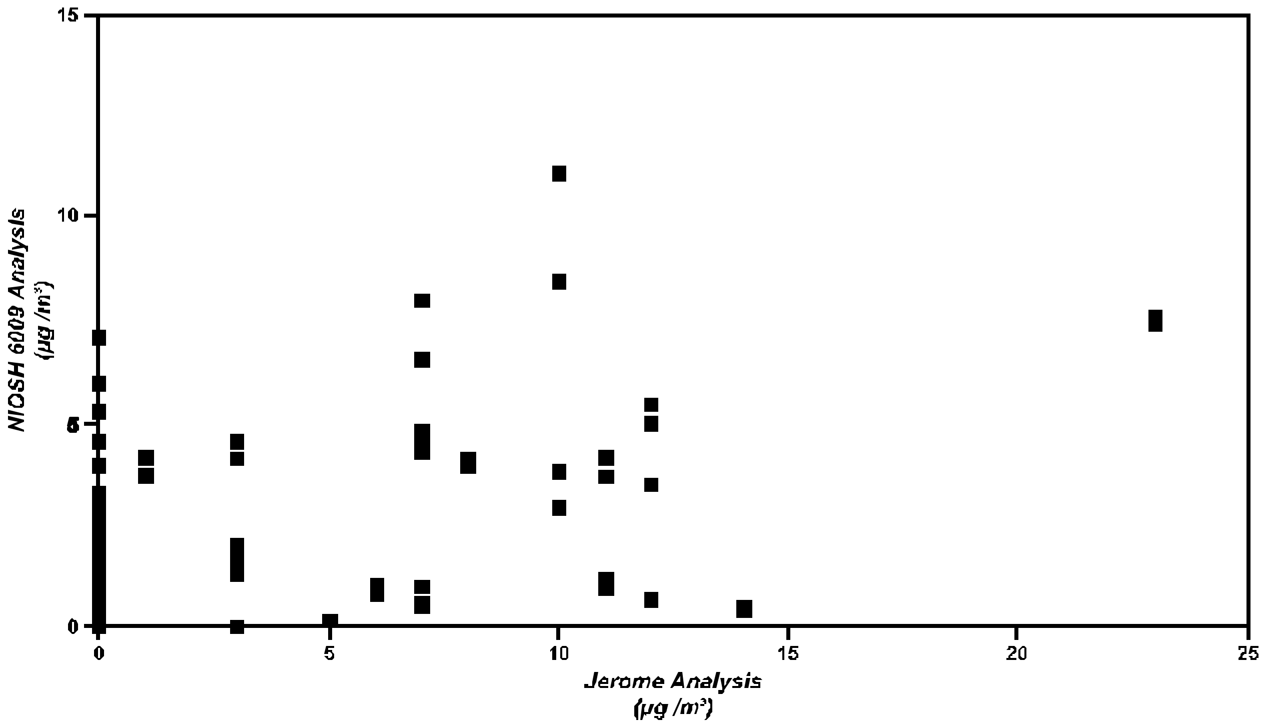

Figure 2. Statistical Pairwise Comparison of Mercury Levels

STATISTICAL COMPARISON METHOD

Figure 2 shows a comparison of data points from the Jerome Mercury Vapor Analyzer with data from the modified NIOSH Method 6009 laboratory analysis [(2)]. A statistical pairwise comparison method was used to compare data from the two mercury measurement methods.

Both data sets were analyzed to determine if the data fit a normal distribution model. Since neither the field test data nor the laboratory test data fit normal distribution curves, the data were tested about the median rather than the mean. A total of 204 observations was obtained. Pairwise analysis[(3)] indicated that both the Jerome and NIOSH data sets were significantly different. The probability value (p) was 0.0327, which was less than the significance level of 0.05. The Spearman correlation coefficient, R, was 0.420, indicating that the data sets were not correlated. (R values approach ±1.0 with increasing degrees of correlation.) One possible explanation for the lack of correlation is the relatively large degree of uncertainty associated with measuring low levels of mercury with the Jerome analyzer. The modified NIOSH method consistently detected measurable amounts of mercury when concentrations were below the Jerome detection limit of approximately 3 µg/m^3. Statistical comparisons of data taken at other mercury spill sites indicated highly comparable results for the Jerome instrument and the modified NIOSH 6009 method.

RESULTS AND DISCUSSION

As shown in Table 1, the Jerome analyzer was effective in identifying "hot spots" where the mercury concentration was greatest, enabling workers to prioritize areas for initial decontamination efforts. As the cleanup efforts progressed, the mercury levels in the indoor air dropped rapidly below the level detectable using the Jerome analyzer.

The modified NIOSH Method 6009 produced results that were consistently lower than the corresponding Jerome analyzer readings (except when the Jerome readings were off the low end of the scale). Given the fact that NIOSH Method 6009 was modified specifically to have a working range extending to very low concentrations, the results from this method are a more accurate reflection of the mercury vapor levels at each location. A comparison of readings from the Jerome analyzer and the modified NIOSH 6009 Method is illustrated in Figure 3.

The results of the duplicate samples analyzed by the Florida Department of Health and commercial laboratories were in excellent agreement with those from the laboratory using modified methods.

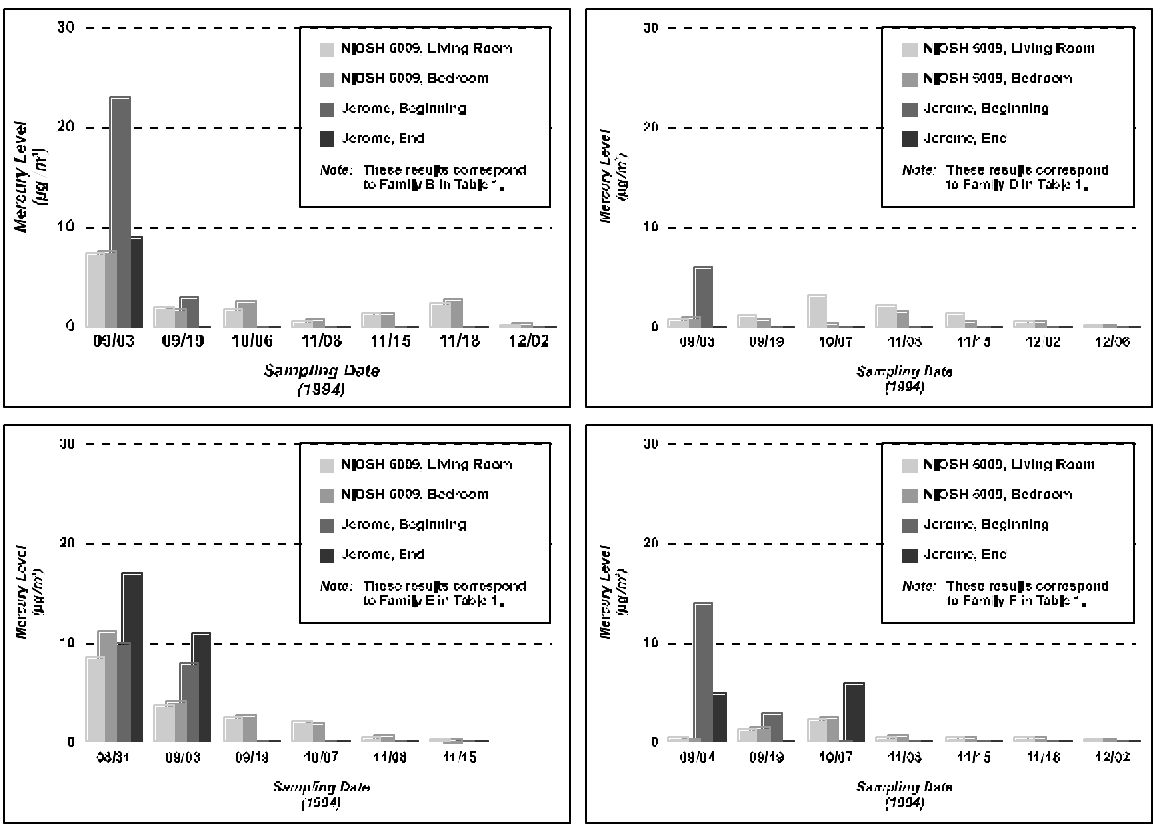

Figure 3. Mercury Levels Measured in Four Representative Houses

CONCLUSIONS

NIOSH Method 6009 has been modified to use more concentrated analyte solutions for cold vapor Atomic Absorption analysis. This was demonstrated to be an effective way of measuring low levels of metallic mercury in indoor air samples. Matrix effects for analyzing samples were minimized by using sorbent material for the preparation of blanks and calibration standards. The modified NIOSH method is simple enough to enable rapid sample turnaround, an important factor in making timely decisions. The procedure conforms to accepted methodologies and QA/QC procedures.

ACKNOWLEDGMENTS AND DISCLAIMER

The authors wish to thank Nancy McGuire and Beth A. Luhman of REAC for their editorial and design support. The analytical method was developed to meet U.S. EPA/ERT/REAC laboratory requirements to monitor indoor metallic mercury vapor and may not be applicable to the activities of other organizations. Mention of trade names or commercial products does not constitute endorsement or recommendation for their use.

REFERENCES

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Table 1. Mercury Levels in Micrograms per Cubic Meter ($\mu g/m^3$)

	Jerome		NIOSH 6009		Date		Jerome		NIOSH 6009		Date
Family	**Beg.**	**End**	**LR**	**BR**	**(1994)**	**Family**	**Beg.**	**End**	**LR**	**BR**	**(1994)**
A	80.00	81.00	43.63	26.73	08/31	D	6.00	ND	0.79	0.97	09/03
	11.00	10.00	4.10	3.62	09/03		ND	ND	1.18	0.89	09/19
	7.00	5.00	4.76	4.23	09/19		ND	ND	3.11	0.37	10/07
	ND	61.00	5.95	5.25	10/06		ND	ND	2.08	1.59	11/08
	ND	ND	1.04	1.04	11/08		ND	ND	1.45	0.55	11/15
	ND	ND	0.22	0.21	11/15		ND	ND	0.53	0.59	12/02
B	23.00	9.00	7.39	7.54	09/03		ND	ND	0.08	0.06	12/16
	3.00	ND	1.97	1.86	09/19	E	10.00	17.00	8.44	11.14	08/31
	ND	ND	1.71	2.44	10/06		8.00	11.00	3.89	4.06	09/03
	ND	ND	0.53	0.73	11/08		ND	ND	2.53	2.66	09/19
	ND	ND	1.21	1.2	11/15		ND	ND	2.03	1.95	10/07
	ND	ND	2.21	2.8	11/18		ND	ND	0.65	0.76	11/08
	ND	ND	0.16	0.25	12/02		ND	ND	0.24	0.28	11/15
C	ND	ND	4.52	7.10	08/31	F	14.00	5.00	0.41	0.33	09/04
	ND	ND	0.43	0.18	09/04		3.00	ND	1.28	1.53	09/19
	ND	ND	0.56	1.11	09/19		ND	6.00	2.22	2.67	10/07
	ND	ND	0.73	1.23	10/04		ND	ND	0.49	0.65	11/08
	ND	ND	0.64	1.67	10/07		ND	ND	0.30	0.30	11/15
	ND	ND	0.56	0.84	10/08		ND	ND	0.44	0.41	11/18
	ND	ND	0.21	0.36	11/15		ND	ND	0.24	0.26	12/02
	ND	ND	0.18	0.38	11/18						
	ND	ND	0.27	0.53	11/21						
	ND	ND	0.16	0.45	12/02						
	ND	ND	0.07	0.08	12/16						

Beg. = Beginning of sampling　　LR = Living Room　　ND = Not detected

End = End of sampling　　BR = Bedroom