American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

A comparison of four personal sampling methods for the determination of mercury vapor

CHARLES S. McCAMMON , STEVEN L. EDWARDS , R. DeLON HULL & WILLIAM J. WOODFIN

To cite this article: CHARLES S. McCAMMON , STEVEN L. EDWARDS , R. DeLON HULL & WILLIAM J. WOODFIN (1980) A comparison of four personal sampling methods for the determination of mercury vapor, American Industrial Hygiene Association Journal, 41:7, 528-531, DOI: 10.1080/15298668091425202

To link to this article: https://doi.org/10.1080/15298668091425202

In Table I we present the ratio of the product, solvent concentration times sample thickness, for the glove material which least resisted penetration to that which most resisted penetration. This ratio is never less than two, and in one case is as high as 48. It is also important to realize that if a glove from manufacturer A best resists penetration from one solvent, it is not necessarily the one which will best resist penetration from another solvent.

These data demonstrate that there may be significant differences in performance between glove materials of the same nominal composition from different manufacturers. The differences may result from minor differences in formulation between manufacturers, or from variations in treatment which may alter polymer network orientation or cross-link densities. Whatever the reason, the prudent course when assessing protective clothing performance is to test samples from several suppliers with the solvents one plans to use.

acknowledgements

We thank C. Riggs for the statistical analyses and J. Orbon for technical assistance.

references

1. **Weeks, R.W., Jr. and B.J. Dean**: Permeation of Methanolic Aromatic Amine Solutions Through Commercially Available Glove Materials. *Am. Ind. Hyg. Assoc. J. 38*:721-725 (1977).

2. **Sansone, E.B. and Y.B. Tewari**: The Permeability of Laboratory Gloves to Selected Solvents. *Am. Ind. Hyg. Assoc. J. 39*:169-174 (1978).

3. **Sansone, E.B. and Y.B. Tewari**: The Permeability of Laboratory Gloves to Selected Nitrosamines, pp. 517-529. In *Environmental Aspects of N-Nitroso Compounds,* (E.A. Walker, M. Castegnaro, L. Griciute and R.E. Lyle, eds.) Lyon, International Agency for Research on Cancer (1978).

4. **Sansone, E.B. and Y.B. Tewari**: Penetration of Protective Clothing Materials by 1,2-Dibromo-3-chloropropane, Ethylene Dibromide, and Acrylonitrile. *Am. Ind. Hyg. Assoc. J. 39*:921-922 (1978).

5. **U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health:** *Development of Performance Criteria for Protective Clothing Used Against Carcinogenic Liquids,* Publication No. 79-106, U.S. Government Printing Office, Washington, D.C. (1978).

A comparison of four personal sampling methods for the determination of mercury vapor

CHARLES S. McCAMMON, Jr.[A], STEVEN L. EDWARDS[C], R. DeLON HULL[B] and WILLIAM J. WOODFIN[B]
[A]National Institute for Occupational Safety and Health, Division of Surveillance, Hazard Evaluation, and Field Studies, [B]Division of Physical Sciences and Engineering, 4676 Columbia Parkway, Cincinnati, Ohio 45226;
[C]Occupational Safety and Health Administration, Analytical Laboratory, 390 Wakara Way, Salt Lake City, Utah 84108

Four sampling and analytical methods for mercury vapor were compared to each other in terms of precision and accuracy. The four sampling medias used were the 3M passive Mercury Vapor Monitor, the Los Alamos tandem sampling tube, the hopcalite tube, and the iodine impregnated charcoal tube. Six samples from each method were collected at nominal mercury concentrations of 0.05, 0.1, and 0.2 mg/m^3. The hopcalite and 3M monitors gave comparable results at all three concentrations while the Los Alamos method gave similar results at the two highest concentrations. The iodine charcoal tube method was the only one exhibiting poor precision when tube loadings were less than 3 μg of mercury.

introduction

There have been reported in the literature(1-4) several methods for the determination of personal exposure to mercury vapor. Since more than one of these methods are currently being used by OSHA and NIOSH, a short study was conducted to compare four different sampling and analytical methods for elemental mercury vapor to determine how well these methods compare to one another. The four methods tested were the 3M passive Mercury Vapor Monitoring System,(1,5) the tandem mercury sampling tube method developed by the Los Alamos Scientific Laboratories (LASL),(2) the hopcalite tube method,(3) and the iodine impregnated charcoal tube method.(4)

experimental

sampling media

The 3M Mercury Monitors were obtained from and analyzed by 3M, St. Paul, Minnesota. The LASL tandem sampling tubes and the hopcalite tubes were purchased from SKC, Inc., Eighty-Four, Pennsylvania and the iodine impregnated charcoal tubes were purchased from Mine Safety Appliances Company, Pittsburgh, Pennsylvania.

sample generation

A dynamic generation system was used to generate nominal concentrations of 0.05, 0.1, and 0.2 mg/m^3 of mercury

---

Mention of company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health or by the Occupational Safety and Health Administration.

TABLE I
Summary of Comparison Data

Nominal Concentration mg/m^3		LASL Tubes	3M Monitors	Hopcalite	Iodine-Charcoal
0.05	$\bar{X}$	0.049	0.060	0.059	0.072
	SD	0.003	0.001	0.003	0.022
	COV	0.056	0.020	0.058	0.312
	Loading (μg)	0.1	-	1.2 - 4.4	1.5
0.1	$\bar{X}$	0.109	0.122	0.119	0.115
	SD	0.010	0.001	0.006	0.019
	COV	0.092	0.010	0.046	0.161
	Loading (μg)	0.1	-	1.8 - 3.6	3.0
0.2	$\bar{X}$	0.219	0.218	0.221	0.199
	SD	0.005	0.006	0.006	0.006
	COV	0.021	0.027	0.029	0.032
	Loading (μg)	0.1	-	4.4 - 7.8	6.0

$\bar{X}$ = mean of six samples, mg/m^3
SD = standard deviation, mg/m^3
COV = coefficient of variation

vapor. The generation system was the same one utilized in an earlier mercury method evaluation.(5) The mercury vapor concentration was determined from calculations of the vapor pressure at 20 °C. In the earlier work,(5) the mercury concentration was independently verified using the LASL method. These two values, the calculated and the measured concentration, were found to always be within at least ±10% of each other. For the purposes of this study, a nominal mercury vapor concentration was established from calculations based on vapor pressure and the concentration was held constant throughout the tests. In this way, an exact mercury concentration was not known but a constant source of mercury vapor was established so that the four methods could be compared to each other.

All four of the sampling devices were exposed simultaneously to the same mercury vapor atmosphere. At each of the three mercury concentrations, six replicate samples of each method were exposed. The 3M Monitors were exposed in a special exposure chamber which was on loan from 3M and had been previously described.(5) A continuous direct-reading UV absorption monitor was used to insure that the mercury concentration did not vary over the course of the 8-hour test run.

The six 3M Monitors were continuously exposed for 8 hours while sample tubes from the other three methods were collected for various periods throughout the day until six samples of each type had been exposed. From the recorder trace of the UV mercury instrument, the fluctuations of mercury concentrations were no more than ±0.002 mg/m^3, thus the samples collected throughout the day were assumed to be identical.

The LASL tubes were collected at 100 cc/min for total volumes of 0.5-2.0 L, resulting in a constant loading of approximately 100 ng of mercury per tube. The hopcalite tubes were sampled at 1 Lpm for various times in order to vary the tube loadings. The total sample volumes varied from 15 to 40 L resulting in tube loadings of 1-7 μg of mercury. The iodine impregnated charcoal tubes were all sampled at 1 Lpm for a total sample volume of 30 liters, resulting in tube loadings of 1.5 to 6.0 μg of mercury.

analytical procedures

3M mercury monitor

The 3M monitors selectively collect elemental mercury vapor via diffusion onto a gold substrate and the sample is quantified by measuring the change in resistance across the gold substrate. As the mercury absorbs on the gold, the resistance across the gold foil changes proportionately to the amount of mercury collected. 3M has developed their system so that the user purchases the monitors, exposes them, and returns them to 3M for analysis. A previous evaluation has shown this method to be both accurate and precise.(5)

LASL tandem sampler

The LASL sampling tube(2) contains a trapping section of Carbosieve B to collect the organic volatile mercury fraction followed by a section of silvered Chromosorb P to collect the elemental mercury vapor. The tube may be preceded with a glass fiber filter to collect particulate species. Analysis of these tubes and filters is a straight forward procedure;

TABLE II
Comparison of LASL Method to the Iodine-Charcoal Method

Nominal Mercury Concentration (mg/m^3)		LASL Tubes	Iodine-Charcoal
0.05	$\bar{X}$	0.066	0.071
	SD	0.003	0.010
	COV	0.038	0.141
	Loading (μg)	0.1	0.5
0.1	$\bar{X}$	0.121	0.136
	SD	0.007	0.029
	COV	0.061	0.213
	Loading (μg)	0.1	1.0
0.2	$\bar{X}$	0.236	0.310
	SD	0.012	0.022
	COV	0.050	0.072
	Loading (μg)	0.1	2.0

$\bar{X}$ = mean of six samples, mg/m^3
SD = standard deviation, mg/m^3
COV = coefficient of variation

however, it requires a special complex thermal desorption unit.(6) After the tube is broken in half, the two sections and the filter are individually analyzed by thermally desorbing the mercury into the absorption cell of a flameless atomic absorption spectrophotometer. This method therefore allows for the determination (as discrete species) of particulate, volatile organic, and elemental mercury, which are collected simultaneously. This method has been demonstrated to give excellent precision and speed of analysis.(6) A detailed description of the thermal desorption unit and analytical procedure is available in the method write-up.(6,7)

hopcalite tubes

Tubes containing 200 mg of hopcalite were used to collect the elemental mercury samples. Hopcalite will also trap volatile organic mercury compounds. The hopcalite was dissolved with concentrated nitric and hydrochloric acid. Stannous chloride was added to an aliquot of the sample to generate mercury vapor from the sample. The mercury vapor was then driven into the absorption cell of a flameless atomic absorption spectrophotometer for analysis.(3)

iodine impregnated charcoal tubes

Elemental and volatile organic mercury vapor is adsorbed in a standard sized charcoal tube (150 mg) filled with a special iodine impregnated charcoal. After collection, the charcoal sample is placed in a tantalum boat which is positioned directly in the flame of an atomic absorption spectrophotometer. As the charcoal is heated, the collected mercury vapor is driven into the AA where it is analyzed.(4)

advantages and disadvantages of the methods

Each method has some advantages and disadvantages depending on the need and analytical capabilities of the user. For someone who needs to monitor for only elemental mercury vapor and has little or no analytical capabilities, then the 3M Mercury Vapor Monitor is ideal. The collection device is small, lightweight, and does not require a personal sampling pump. The analysis of these passive monitors is provided by 3M at a very reasonable cost. The 3M monitors cannot be used to monitor for organic mercury contaminants and there can be a negative interference from chlorine gas in the collection of mercury vapor.(5)

The iodine impregnated charcoal tube and the hopcalite tube methods can both be used to monitor for total volatile mercury exposure. If there are particulate mercury compounds present in the environment, an unknown portion of the aerosol will be trapped by the separation plugs in the tubes. However, the collection of aerosols is not quantitative. The analytical procedure used with the hopcalite tube requires only a flameless AA unit and assorted common glassware. For the iodine charcoal tube method, a tantalum boat and an atomic absorption spectrophotometer are required. The analysis of the iodine charcoal tubes appears to be more operator and technique dependent than does that of the hopcalite tubes.

The LASL tube is preceded by a 13-mm glass fiber filter and is capable of collecting particulate, organic and elemental mercury compounds. The sampling train is such that the three forms of mercury compounds can also be analyzed separately. The LASL method is the only one with this capability. The analysis of the LASL tube requires a special and not commerically available desorption apparatus. The desorption device is followed by a flameless AA analyzer. So if one can set up the thermal desorption apparatus and has access to a flameless AA, the LASL method offers the greatest flexibility for all forms of mercury compounds.

discussion and results

A summary of the data collected is presented in Table I. One-factor analysis of variance was used to compare the means of the methods at each concentration. When comparing the means as a group, at $p < 0.01$, there was no significant difference found even at a mercury vapor concentration of 0.05 mg/m^3. However, if the means of each method are compared individually to the other means, then differences can be seen. At a mercury vapor concentration of 0.05 mg/m^3 and at $p < 0.05$, a significant difference can be seen between the average results of the LASL and the iodine charcoal methods. No other means when compared two at a time showed any significant differences. At mercury concentrations of 0.1 and 0.2 mg/m^3, there were no significant differences in any of the means at a level of $p < 0.05$.

In looking at the variability of the data, a Fmax test was applied to the group variances. At 0.05 and 0.1 mg/m^3, at a significance level of 95%, the data were found to be heterogeneous, *i.e.*, there was a significant difference in the variability. At the 0.2 mg/m^3 mercury concentration, the variances showed no significant differences (homogeneous). When the iodine charcoal tube data are deleted from the test, the variances of the data at 0.05 and 0.1 mg/m^3 show no significant differences. Therefore, it can be concluded that the variability of the iodine charcoal tube data is significantly different from that of the other three methods. This might have been surmised after a visual inspection of the data since the coefficient of variation for iodine charcoal method is 31.2% at a mercury concentration of 0.05 mg/m^3.

This finding is in agreement with data collected just prior to this study where the iodine charcoal tube method was compared to the LASL method at levels of 0.05, 0.1, and 0.2 mg/m^3 of mercury. The results of this study are summarized in Table II. As can be seen from these data, at low loadings of mercury on the iodine charcoal tubes, 1 μg or less, the precision of the method is poor. Only at higher loadings of around 3 μg of mercury per tube does the precision become acceptable. In this test, there was a significant difference in the variability of the data at mercury concentrations of 0.05 and 0.1 mg/m^3, but not at 0.2 mg/m^3.

For the iodine charcoal tubes, various lots from the same manufacturer were used (lots no. 2, 4, and 10) with no apparent difference in blank values or tube performance. Therefore, it appears that the imprecision of the iodine charcoal method at low tube loadings must be due to the analytical procedure.

summary

Four different personal sampling and analytical methods for mercury vapor were comparatively tested at mercury concentrations of 0.05, 0.1, and 0.2 mg/m^3. The 3M monitor and the hopcalite methods compared quite well to each other at all three concentrations. The LASL method compared closely to the 3M monitor and hopcalite method at the highest mercury concentration and gave results only slightly lower at the other two concentrations. All three methods exhibited good precision over the concentration range of 0.05 - 0.2 mg/m^3. The iodine charcoal method compared well to the other methods at the 0.2 and 0.1 mg/m^3 concentrations but gave results significantly higher at the 0.05 mg/m^3 level. At loadings of less than about 3 μg per tube, the precision of the iodine charcoal method was poor.

acknowledgements

Thanks go to Dave Braun of 3M for providing the mercury monitors and their analysis.

references

1. **Braun, D.L.:** *Personal Monitoring of Mercury Vapor Exposures.* ICESA, Volume 2, IEEE Catalogue #75-CH 1004-1 (1976).
2. **Trujillo, P.E. and E.E. Campbell:** Development of a Multistage Air Sampler for Mercury. *Anal. Chem. 47*:1629 (1975).
3. **Rathje, A.O. and D.H. Marcero:** Improved Hopcalite Procedure for the Determination of Mercury Vapor in Air by Flameless Atomic Absorption. *Am. Ind. Hyg. Assoc. J. 37*:331 (1976).
4. **Moffitt, A.E., Jr. and R.E. Kupel:** A Rapid Method Employing Impregnated Charcoal and Atomic Adsorption Spectroscopy for the Determination of Mercury. *Am. Ind. Hyg. Assoc. J. 32*:614 (1971).
5. **McCammon, C.S., Jr. and J.W. Woodfin:** An Evaluation of a Passive Monitor for Mercury Vapor. *Am. Ind. Hyg. Assoc. J. 38*:378 (1977).
6. **NIOSH:** *Manual of Analytical Methods, Volume 4, Second Edition.* U.S. Government Printing Office, #757-141/1829. Method #S199.
7. **NIOSH:** *Manual of Analytical Methods, Volume 1, Second Edition.* U.S. Government Printing Office, #017-033-00267-3. Method #P&CAM 175.

Comparison of methods for determination of desorption efficiencies

JAN KRAJEWSKI, JAN GROMIEC and MAREK DOBECKI
Institute of Occupational Medicine, ul. Teresy 8, 90-950 Lodz, Poland

Three methods for desorption efficiency determination were compared with a reference dynamic method for 12 compounds. Only one of them gave values that were statistically different. The method, in which standard solutions of determined compounds in CS_2 are injected onto charcoal, is recommended to all laboratories dealing with air analysis as it is simpler than the dynamic method. Independence of the desorption efficiency on charcoal loading was also confirmed. The desorption efficiencies for individual compounds and their mixtures were found to be different.

introduction

Since charcoal tubes were used by White$^{(1)}$ for collection of air samples, the method has found application in many countries. However, versions of the method being used differ in the determination of desorption efficiencies of collected material from charcoal.$^{(2-5)}$ Since the desorption efficiency influences the final result of air analysis, the knowledge of differences in values obtained by separate methods becomes extremely important.

In the literature, several works on organic vapor adsorption by charcoal and subsequent recovery are reported. Investigated were: results obtained with different types of tubes,$^{(6)}$ influence of accompanying compounds on desorption efficiency,$^{(7)}$ breakthrough time at different sampling rates, concentration and air volume,$^{(8)}$ effects of humidity on adsorption,$^{(6-8)}$ stability of samples with time,$^{(8)}$ and variation in data obtained by individual laboratories.$^{(9)}$