

**WAC 296-62-07660 Appendix D to WAC 296-62-076—Sampling and analytical methods for MDA monitoring and measurement procedures.** Measurements taken for the purpose of determining employee exposure to MDA are best taken so that the representative average eight-hour exposure may be determined from a single eight-hour sample or two four-hour samples. Short-time interval samples (or grab samples) may also be used to determine average exposure level if a minimum of five measurements are taken in a random manner over the eight-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random samples taken on one work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

There are a number of methods available for monitoring employee exposures to MDA. The method WISHA currently uses is included below.

The employer, however, has the obligation of selecting any monitoring method which meets the accuracy and precision requirements of the standard under his/her unique field conditions. The standard requires that the method of monitoring must have an accuracy, to a ninety-five percent confidence level, of not less than plus or minus twenty-five percent for the select PEL.

WISHA methodology.

Sampling procedure.

Apparatus:

Samples are collected by use of a personal sampling pump that can be calibrated within  $\pm 5$  percent of the recommended flow rate with the sampling filter in line.

Samples are collected on 37 mm Gelman type A/E glass fiber filters treated with sulfuric acid. The filters are prepared by soaking each filter with 0.5 mL of 0.26N  $H_2SO_4$ . (0.26 N  $H_2SO_4$  can be prepared by diluting 1.5 mL of 36N  $H_2SO_4$  to 200 mL with deionized water.) The filters are dried in an oven at 100 degrees C. for one hour and then assembled into three-piece 37 mm polystyrene cassettes without backup pads. The front filter is separated from the back filter by a polystyrene spacer. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.

After sampling, the filters are carefully removed from the cassettes and individually transferred to small vials containing approximately 2 mL deionized water. The vials must be tightly sealed. The water can be added before or after the filters are transferred. The vials must be sealable and capable of holding at least 7 mL of liquid. Small glass scintillation vials with caps containing Teflon liners are recommended.

Reagents:

Deionized water is needed for addition to the vials.

Sampling technique:

Immediately before sampling, remove the plastic plugs from the filter cassettes.

Attach the cassette to the sampling pump with flexible tubing and place the cassette in the employee's breathing zone.

After sampling, seal the cassettes with plastic plugs until the filters are transferred to the vials containing deionized water.

At some convenient time within ten hours of sampling, transfer the sample filters to vials.

Seal the small vials lengthwise.

Submit at least one blank filter with each sample set. Blanks should be handled in the same manner as samples, but no air is drawn through them.

Record sample volumes (in L of air) for each sample, along with any potential interferences.

Retention efficiency:

A retention efficiency study was performed by drawing 100 L of air (eighty percent relative humidity) at 1 L/min through sample filters that had been spiked with 0.814 microgram MDA. Instead of using backup pads, blank acid-treated filters were used as backups in each cassette. Upon analysis, the top filters were found to have an average of 91.8 percent of the spiked amount. There was no MDA found on the bottom filters, so the amount lost was probably due to the slight instability of the MDA salt.

Extraction efficiency:

The average extraction efficiency for six filters spiked at the target concentration is 99.6 percent.

The stability of extracted and derivatized samples was verified by re-analyzing the above six samples the next day using fresh standards. The average extraction efficiency for the reanalyzed samples is 98.7 percent.

Recommended air volume and sampling rate:

The recommended air volume is 100 L.

The recommended sampling rate is 1 L/min.

Interferences (sampling):

MDI appears to be a positive interference. It was found that when MDI was spiked onto an acid-treated filter, the MDI converted to MDA after air was drawn through it.

Suspected interferences should be reported to the laboratory with submitted samples.

Safety precautions (sampling):

Attach the sampling equipment to the employees so that it will not interfere with work performance or safety.

Follow all safety procedures that apply to the work area being sampled.

Analytical procedure:

Apparatus: The following are required for analysis.

A GC equipped with an electron capture detector. For this evaluation a Hewlett Packard 5880 Gas Chromatograph equipped with a Nickel 63 High Temperature Electron Capture Detector and a Linearizer was used.

A GC column capable of separating the MDA derivative from the solvent and interferences. A 6 ft X 2 mm ID glass column packed with three percent OV-101 coated on 100/120 Gas Chrom Q or a 25 meter DB-1 or DB-5 capillary column is recommended for this evaluation.

A electronic integrator or some other suitable means of measuring peak areas or heights.

Small resealable vials with Teflon-lined caps capable of holding 4 mL.

A dispenser or pipet for toluene capable of delivering 2.0 mL.

Pipets (or repipets with plastic or Teflon tips) capable of delivering 1 mL for the sodium hydroxide and buffer solutions.

A repipet capable of delivering 25 micro-L HFAA.

Syringes for preparation of standards and injection of standards and samples into a GC.

Volumetric flasks and pipets to dilute the pure MDA in preparation of standards.

Disposable pipets to transfer the toluene layers after the samples are extracted.

Reagents:

0.5 NaOH prepared from reagent grade NaOH.

Toluene, pesticide grade. Burdick and Jackson distilled in glass toluene was used.

Heptafluorobutyric acid anhydride (HFAA). HFAA from Pierce Chemical Company was used.

pH 7.0 phosphate buffer, prepared from 136 g potassium dihydrogen phosphate and 1 L deionized water. The pH is adjusted to 7.0 with saturated sodium hydroxide solution.

4,4'-Methylenedianiline (MDA), reagent grade.

Standard preparation:

Concentrated stock standards are prepared by diluting pure MDA with toluene. Analytical standards are prepared by injecting uL amounts of diluted stock standards into vials that contain 2.0 mL toluene.

25 µL HFAA are added to each vial and the vials are capped and shaken for 10 seconds.

After ten min, 1 mL of buffer is added to each vial.

The vials are recapped and shaken for ten seconds.

After allowing the layers to separate, aliquots of the toluene (upper) layers are removed with a syringe and analyzed by GC.

Analytical standard concentrations should bracket sample concentrations. Thus, if samples fall out of the range of prepared standards, additional standards must be prepared to ascertain detector response.

Sample preparation:

The sample filters are received in vials containing deionized water.

1 mL of 0.5N NaOH and 2.0 mL toluene are added to each vial.

The vials are recapped and shaken for ten min.

After allowing the layers to separate, approximately 1 mL aliquots of the toluene (upper) layers are transferred to separate vials with clean disposable pipets.

The toluene layers are treated and analyzed.

Analysis:

GC conditions

Zone temperatures:

Column—220 degrees C.  
Injector—235 degrees C.  
Detector—335 degrees C.  
C Gas flows, N<sub>2</sub> Column—30 mL/min  
He Column 0.9 mL/min. (capillary) with  
30 mL/min. Ar/CH<sub>4</sub> (95/5) makeup gas  
Injection volume: 5.0 uL  
Column: 6 ft X 1/8 in ID glass, 3% OV-101 on  
100/120 Gas Chrom Q or 25 meter x .25 mm  
DB-1 or DB-5 capillary  
Retention time of MDA derivative: 2.5 to 3.5,  
depending on column and flow

Chromatogram:

Peak areas or heights are measured by an integrator or other suitable means.

A calibration curve is constructed by plotting response (peak areas or heights) of standard injections versus ug of MDA per sample. Sample concentrations must be bracketed by standards.

Interferences (analytical):

Any compound that gives an electron capture detector response and has the same general retention time as the HFAA derivative of MDA is a potential interference. Suspected interferences reported to the laboratory with submitted samples by the industrial hygienist must be considered before samples are derivatized.

GC parameters may be changed to possibly circumvent interferences.

Retention time on a single column is not considered proof of chemical identity. Analyte identity should be confirmed by GC/MS if possible.

Calculations:

The analyte concentration for samples is obtained from the calibration curve in terms of ug MDA per sample. The extraction efficiency is one hundred percent. If any MDA is found on the blank, that amount is subtracted from the sample amounts. The air concentrations are calculated using the following formulae:  $\text{Microgram/m}^3 = (\text{microgram MDA per sample}) / (1000) / (\text{L of air sampled})$   $\text{ppb} = (\text{microgram/m}^3) (24.46) / (198.3) = (\text{microgram/m}^3) (0.1233)$  where 24.46 is the molar volume at 25 degrees C. and 760 mm Hg.

Safety precautions (analytical):

Avoid skin contact and inhalation of all chemicals.

Restrict the use of all chemicals to a fume hood if possible.

Wear safety glasses and a lab coat at all times while in the lab area.

[Statutory Authority: Chapter 49.17 RCW. WSR 93-04-111 (Order 92-15), § 296-62-07660, filed 2/3/93, effective 3/15/93.]