**3M COMPANY**
**OCCUPATIONAL HEALTH AND ENVIRONMENTAL SAFETY DIVISION**
**DETERMINATION OF FORMALDEHYDE VAPORS IN AIR**
**USING 3M 3721 FORMALDEHYDE MONITORS**
**May, 2002**

## SCOPE

This procedure covers the method of collecting and analyzing samples to determine the amount of formaldehyde present in the air using the 3M 3721 Formaldehyde Monitor. The calibration curve covers the 0-15 microgram range.

## SUMMARY OF THE METHOD

In the monitor, formaldehyde vapors are adsorbed on bisulfite impregnated paper and desorbed with formaldehyde-free distilled water. Aliquots are reacted with chromotropic acid in the presence of sulfuric acid to form a purple monocationic chromogen.[1] The absorbance of the colored solution is read in a spectrophotometer at 580 nanometers (nm) and is proportional to the amount of formaldehyde in the solution.

## APPARATUS

Spectrophotometer - Milton Roy Spectronic 21D or equivalent.

## REAGENTS/SUPPLIES

The following or equivalent reagents and supplies are used:

3M 3721 Formaldehyde Monitor

Chromotropic Acid Solution - Dissolve 0.25 g of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt dihydrate (Aldrich 21,327-6 or equivalent) in 25 mL of formaldehyde-free distilled water. Make solution fresh each day. Previously used Acros 40525-0100, formerly Kodak 230, is no longer available, but existing supplies may be used.

Sulfuric Acid - Concentrated, reagent grade.

Distilled Water - Formaldehyde-free.

1% Sodium Bisulfite Solution - Dissolve 2.5 g of sodium bisulfite (Baker 3556-01 or equivalent) in 250 mL of distilled water.

Standard Formaldehyde Solution - 25 uL of 37% formaldehyde (Aldrich 25,254-9 or equivalent) is diluted to 10 mL with 1% sodium bisulfite solution. This solution is used to prepare the calibration curve - each microliter is equivalent to one microgram of formaldehyde.

## SAMPLING

The monitor is removed from the package and assembled according to the instructions in the package. The following information should be recorded:

1. Monitor number
2. Date of exposure
3. Employee or area identification
4. Temperature and relative humidity
5. Start and stop times
6. Any potential interferences, such as phenol
7. Any comments or unusual circumstances

When personal sampling is being performed, the monitor should be attached near the breathing zone. For area sampling, the monitor should be placed so that at least a 25 fpm face velocity is maintained. The monitor should not be placed in a corner or along a wall where stagnant air may exist. The 3721 monitor is designed for 8-hour sampling and is not recommended for 15-minute STEL sampling.

After sampling, the retaining ring and white barrier film are removed and discarded. The two monitor sections are separated and the bottom section with the clip is discarded. The clear elution cap and primary cup are snapped onto the top section. The ports should be securely sealed with the plugs. A blank control sample should be prepared at the monitoring site and submitted with the samples.

## SAMPLE ANALYSIS

(a) Elution

Both ports of the elution cap are opened and 3 mL of formaldehyde-free distilled water is added to each monitor through the center port using a repipet or syringe. The ports are immediately resealed and each monitor allowed to elute for 30 minutes with occasional gentle agitation. Transfer a 2 mL aliquot of the eluate to a test tube or vial for color development. (The amount of the aliquot may be varied to be sure that each sample absorbance will be within the calibration curve. Dilute the aliquot to 2 mL with 1% sodium bisulfite solution.)

(b) Color Development

Add 1.0 mL of chromotropic acid solution to each sample and mix well. Carefully add 5 mL of concentrated sulfuric acid slowly with mixing. **CAUTION: Take proper safety precautions such as goggles, gloves and apron when handling concentrated sulfuric acid.** Allow the samples to cool to room temperature and measure the absorbance at 580 nm (medium sensitivity setting) using 1 cm cells or 1 in test tube cuvettes. Use distilled water in the reference cell. A reagent blank is carried through all the steps of the sample analysis. Subtract the absorbance of the reagent blank from that of the standards and samples and refer to the calibration curve to determine the micrograms of formaldehyde present.

## CALIBRATION CURVE

To a series of test tubes or vials, carefully add 1.0, 3.0, 5.0, 10.0 and 15.0 microliters of standard formaldehyde solution equivalent to 1.0, 3.0, 5.0, 10.0, and 15.0 micrograms of formaldehyde. Adjust the volumes to 2 mL with 1% sodium bisulfite solution. Develop the color and measure the absorbance as described above. Carry a reagent blank through all the steps and subtract its absorbance from all the standards as well as the samples. Prepare a calibration curve by plotting the corrected absorbance (x axis) vs. micrograms of formaldehyde (y axis). Determine the slope and intercept for the calibration curve.

Appropriate quality control samples are run with each set of standards and samples.

**CALCULATIONS**

(a) $$W = [I + S(A_S - A_b)](3/A)$$

where: W = micrograms of formaldehyde found
$A_S$= absorbance for sample
$A_b$= absorbance for reagent blank
S = slope of the calibration curve
I = intercept of the calibration curve
A = aliquot taken in mL (usually 2 mL)

(b) $$C = \frac{(W - B)(MV)(1000)}{(SR)(r)(t)(MW)}$$

where: C = concentration of formaldehyde in air in ppm
W = micrograms of formaldehyde found
B = micrograms of formaldehyde in the monitor blank
MV= molar volume at given temperature and pressure
(24.45 L/mole at 25$^{o}$C and 760 mm Hg)
MW= molecular weight of formaldehyde (30 amu)
SR = sampling rate for formaldehyde (61.4 $cm^3$/min)
r = recovery (1.0)
t = sampling time in minutes

The above expressions calculate the time-weighted-average concentrations at a sampling temperature of 25 $^{0}$C and pressure of 760 mm Hg. When sampling at other environmental conditions, the concentration need only be corrected for variations in temperature. If the temperature correction is desired, the time-weighted-average concentration can be calculated by mutiplying the concentration calculated above by the temperature correction factor (CFt.)

| Sampling Temperature ($^{0}$C) | ($^{0}$F) | Correction Factor (CFt) |
|---|---|---|
| 44 | 111 | .97 |

| | | |
|---|---|---|
| 37 | 99 | .98 |
| 31 | 88 | .99 |
| 25 | 77 | 1.00 |
| 19 | 66 | 1.01 |
| 13 | 55 | 1.02 |
| 7 | 45 | 1.03 |
| 2 | 36 | 1.04 |
| - 3 | 27 | 1.05 |
| - 8 | 18 | 1.06 |

As shown in the above table, every 10-11 degrees above or below $77^0$F requires a one percent correction to the calculated time-weighted-average concentration. For every $10^0$F increment above $77^0$F, there is a decrease of about 1% in the time-weighted-average concentration. Below $77^0$F, there is an increase in the concentration.

## LIMIT OF QUANTITATION

The routine limit of quantitation (LOQ) is about 1 ug. This results in an air concentration of 0.03 ppm for an 8-hour sample.

## STORAGE

Analysis of spiked monitors after 13 weeks of storage at room temperature showed a recovery of 100.5%.

## DISCUSSION

The precision of the analytical method is reported to be +/-3%.[2]

The precision of the sampling and analytical method has been shown to be +/- 6% in our laboratory. The bias from the midget impinger method has been found to be -3% with a resulting accuracy of 15%.

Both the metatrioxane and paraformaldehyde as well as dimethoxymethane represent positive interferences. Large amounts of phenols cause a negative interference which may completely mask color formation. For monitor samples containing phenol, color development may be accomplished by using 1 mL of 10% chromotropic acid instead of 1% chromotropic acid to decrease the phenol interference, however, the monitor does not collect phenol efficiently and therefore any potential interference is expected to be minimal.[3]

## REFERENCES

1. Methods of Air Sampling and Analysis, Third Edition, J. P. Lodge, Ed., 274 (1989).

2. NIOSH Manual of Analytical Methods, Method No. 3500, Fourth Edition, 1994.

3. Johnson, G. D., 3M Corporate Research Laboratory, Personal Communication.