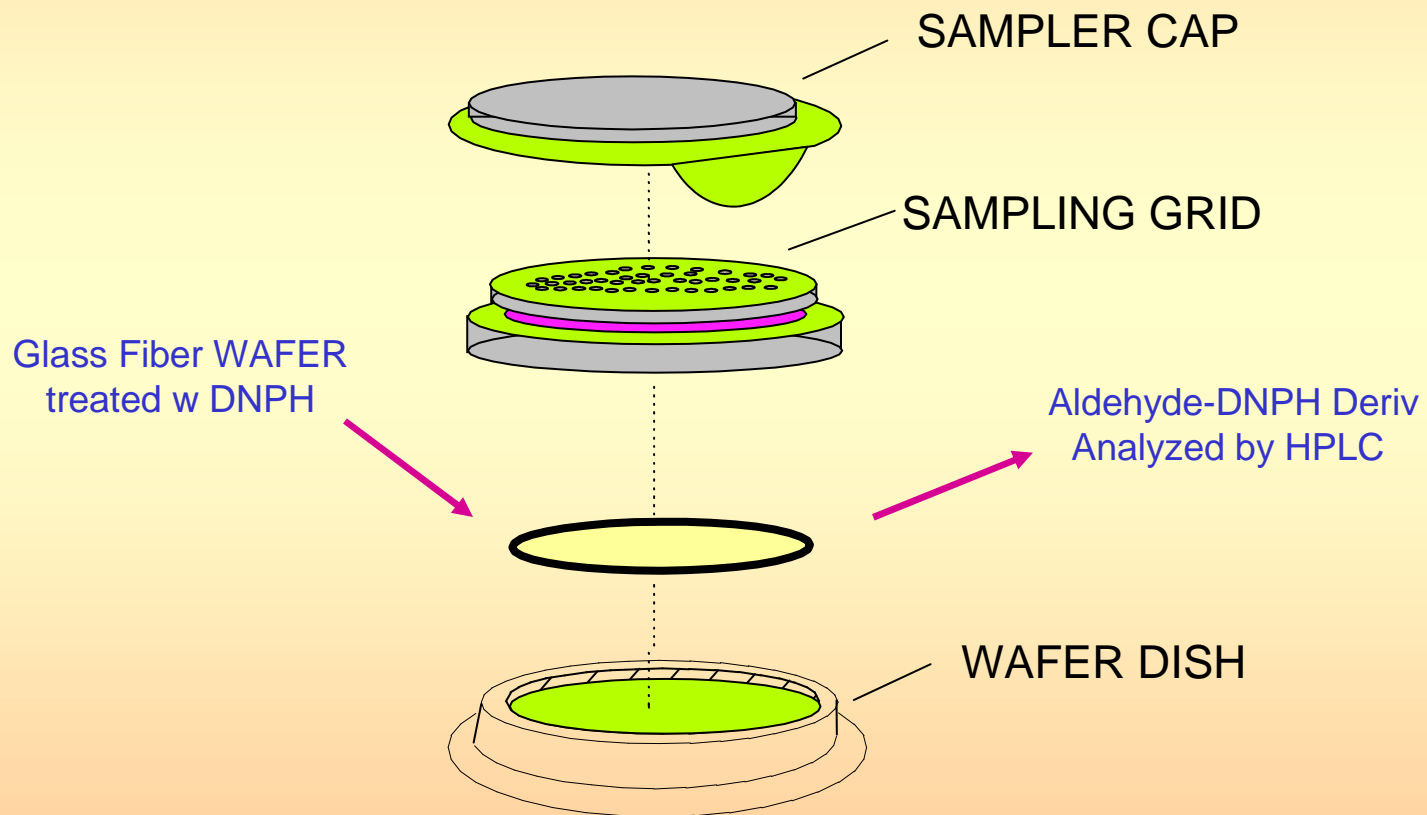


Evaluation of Possible Sampling Error with Formaldehyde Diffusive Samplers

In Health Care Environments

C.R. (Gus) Manning, PhD, CIH

Aldehyde Sampler (schematic)



Analytical Method

Collection Media (sampling tubes):

Silica Gel tube coated with 2,4-dinitrophenylhydrazine reagent

Collection Media (personal monitoring badges):

**Glass Fiber Disc impregnated with stabilizers
and 2,4-dinitrophenylhydrazine reagent**

Analyte:

Formaldehyde (other aldehydes)

Analysis (similar to EPA TO-11):

Extract Wafer - 2ml of 1:1 Acetonitrile/Water (pH 5)

Analyze on C-18 Column. Inj: 50 µg

**Mobile Phase: approx. 50% Acetonitrile / 50% Acetate Buffer
(pH 5)**

HPLC with UV Detector at 350nm

Formaldehyde



FW = **30.03** g/mole

PEL (a) = **0.75** ppm

STEL (b) = **2.0** ppm

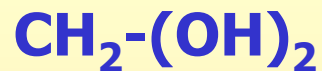
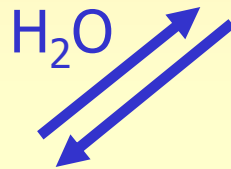
(a) OSHA Permissible (8-hr TWA) Exposure Limit

(b) OSHA Short Term (15-min) Exposure Limit

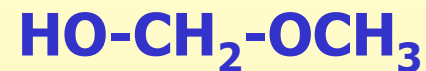
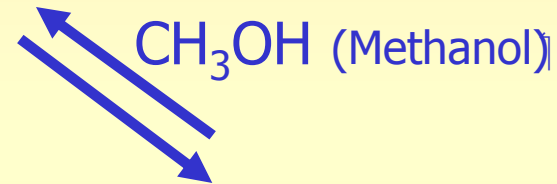
Forms of Formaldehyde



MW = 30.0

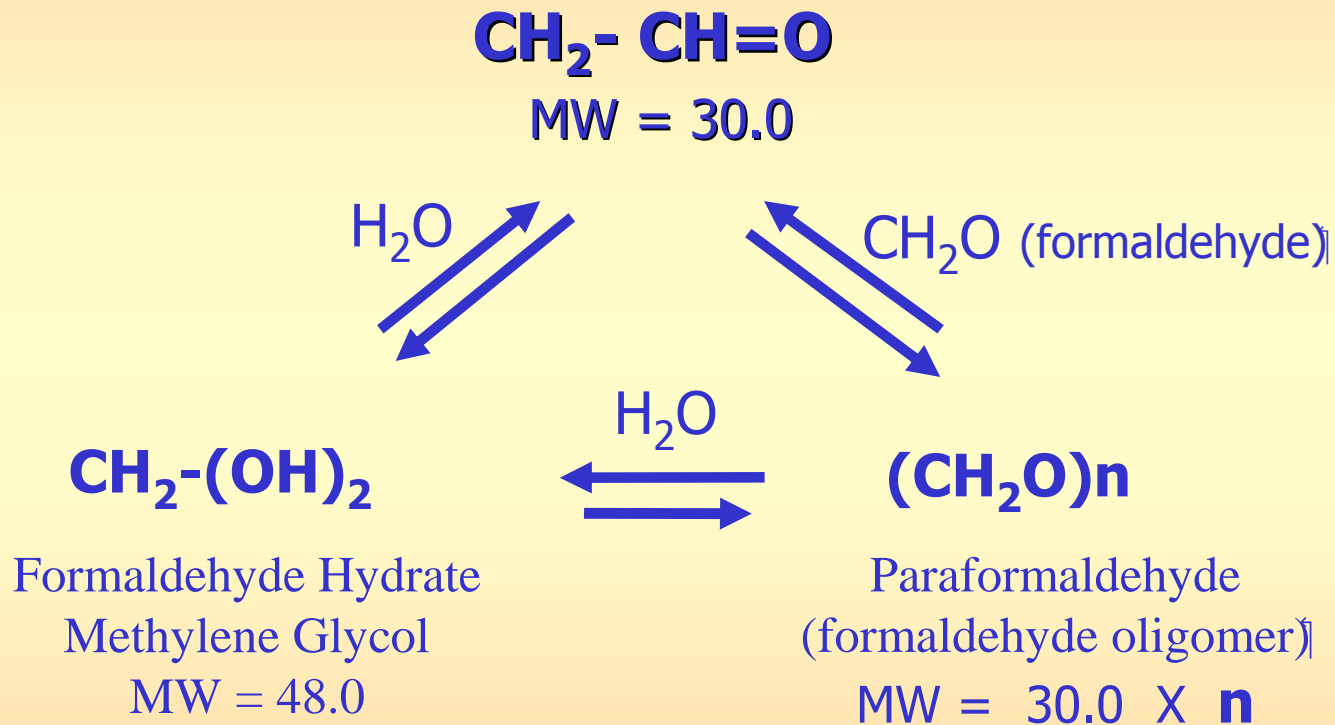


Formaldehyde Hydrate
Methylene Glycol
MW = 48.0



Formaldehyde Methanolate
MW = 62.1

Forms of Formaldehyde



Estimated Sampling Rates for Different Formaldehyde Forms

Formaldehyde Form	Relative Sampling Rate (estimated) (a)
(anhydrous) Formaldehyde MW = 30.0	100%
Formaldehyde Hydrate MW=48.0	79%
Formaldehyde Methanolate MW=62.1	70%
Formaldehyde Dimer MW=60.0	71%

(a) Based on the principle that Sampling Rates are approx. proportional to square root of MW

Formalin

an aqueous solution of formaldehyde

Concentrated Form

36-37% Formaldehyde

10-15% Methanol

54-48% Water

**Commonly used as a reagent
in chemical research
laboratories.**

10% Diluted Form

3 - 4% Formaldehyde

1.0 - 1.5% Methanol

94 - 96% Water

Commonly used as a fixative
in medical diagnostic
laboratories.

Formaldehyde Sampling

(when the source of exposure is formalin)

When the source of exposure to formaldehyde is formalin, OSHA (USA) recommends active sampling unless data are available showing good correlation between active and passive samplers.

OSHA's believes there may be sampling error due to the differing sampling rates of formaldehyde species which may arise from evaporation of formalin.

Calibration of Chambers for Formaldehyde Tests

(using paraformaldehyde)

- OSHA (USA) recommends paraformaldehyde (an oligomer of formaldehyde) as the source of formaldehyde for generating chamber exposures to evaluate air samplers.
- Paraformaldehyde (PFA) is dissolved in warm water, then the solution is evaporated to generate formaldehyde vapor species.
- PFA is recommended because of the belief that evaporation of paraformaldehyde generates only monomer formaldehyde CH_2O .

Plan of Study

A. Formaldehyde Atmospheres Generated from Two Different Sources

- Aqueous Formalin (3.6 % HCHO)
- Aqueous Paraformaldehyde (3.6% HCHO)

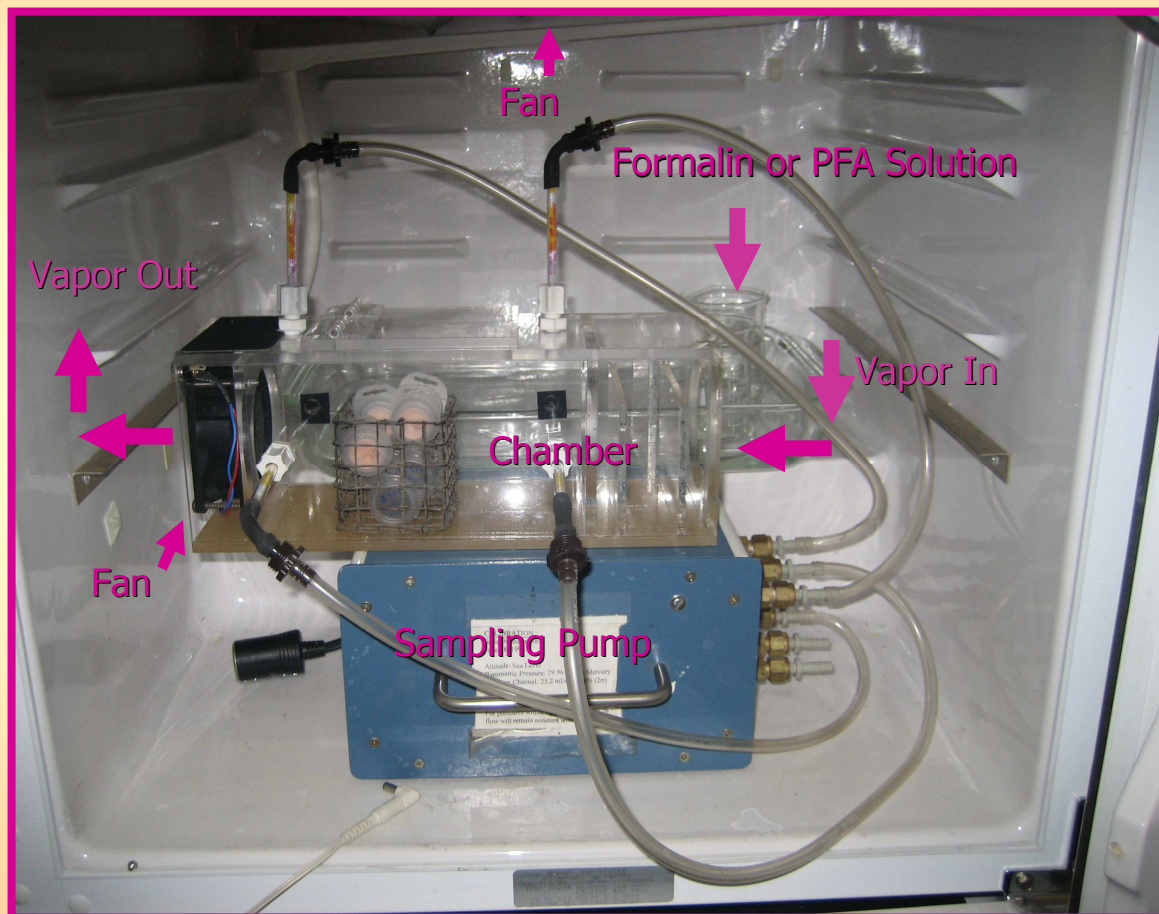
B. Formaldehyde Atmospheres Generated Using 2 Different Methods

- HCHO generated in one-pass through Test Chamber
- HCHO generated and “aged” during multiple passes thru Test Chamber

C. Compare Diffusive Sampling Rates for Formaldehyde

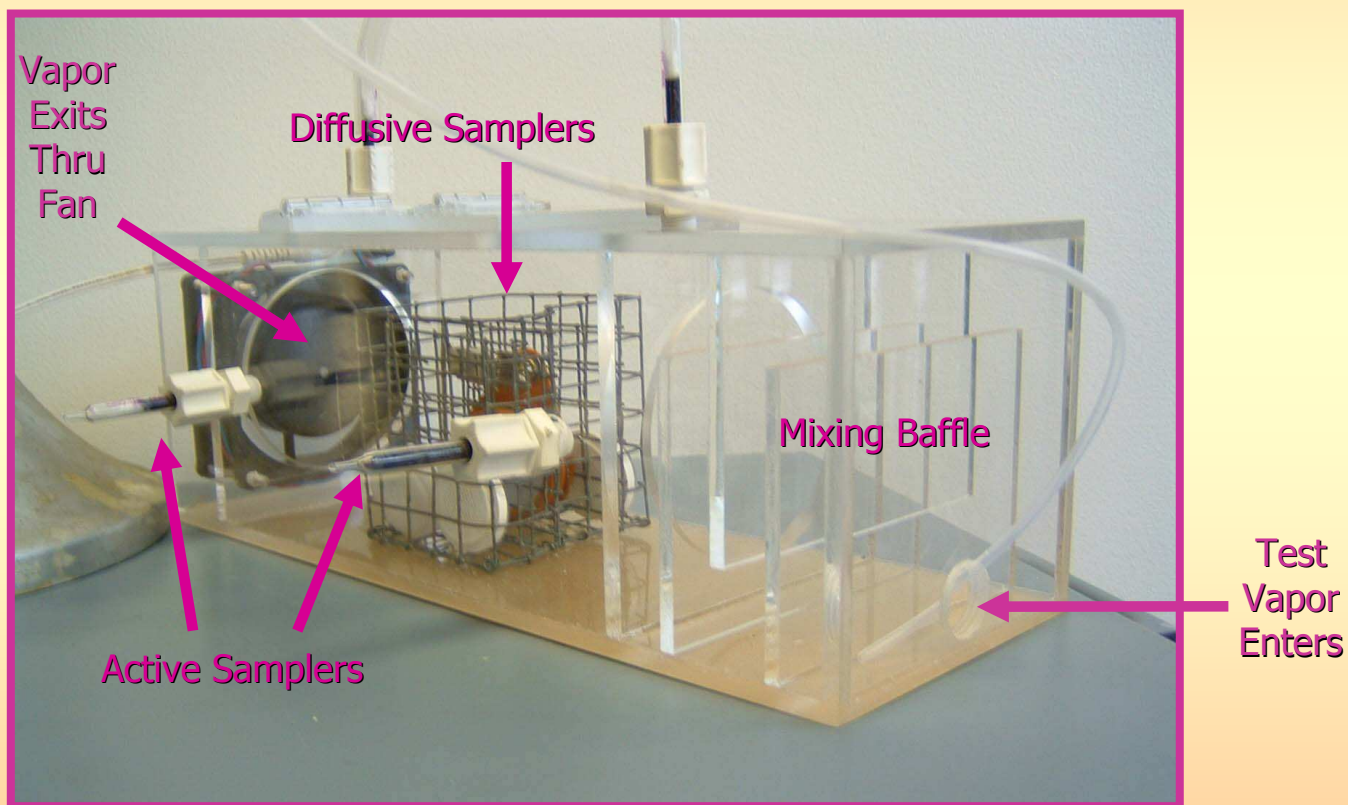
- HCHO generated from Formalin
 - With single-pass of vapor thru Test Chamber
 - Vapor aged with multiple-passes thru Chamber
- HCHO generated from Paraformaldehyde
 - With single-pass of vapor thru Test Chamber
 - Vapor aged with multiple-passes thru Chamber

Exposure Chamber (vapor aged via multiple passes thru Chamber)



Exposure Chamber

(generated vapor makes single pass thru Chamber)



Comparison of Diffusive Sampling Rates (Paraformaldehyde vs Formalin Generation)

Source of Formaldehyde	Chamber Design	HCHO Conc'n by Active Sampling (8hr TWA, ppm)	Sampling Time (min)	Measured Diffusive Sampling Rate (mL/min)	% CV +/-	
Formalin Soln (a)	One Pass Chamber	0.39	62	17.4	23%	
Formalin Soln (a)	One Pass Chamber	1.1	188	13.9	11%	
Formalin Soln (a)	Atmosphere Re-Cycled and Aged	1.4	61	15.1	7%	
Formalin Soln (a)	Atmosphere Re-Cycled and Aged	5.3	277	13.7	5%	
(a) Solution contains 3.6% HCHO				Average for all Formalin Tests =	15.0	11%

Source of Formaldehyde	Chamber Design	HCHO Conc'n by Active Sampling (8hr TWA, ppm)	Sampling Time (min)	Measured Diffusive Sampling Rate (mL/min)	% CV +/-	
Paraformaldehyde Soln (a)	One Pass Chamber	0.36	68	13.5	7	
Paraformaldehyde Soln (a)	One Pass Chamber	0.97	195	13.1	6	
Paraformaldehyde Soln (a)	Atmosphere Re-Cycled and Aged	1.9	135	13.4	6	
Paraformaldehyde Soln (a)	Atmosphere Re-Cycled and Aged	3.7	210	13.3	10	
(a) Solution contains 3.6% HCHO				Average for all Paraformaldehyde Tests =	13.3	1%

Summary of Results

- Measured Diffusive Sampling Rates were near to expected values (13.3 mL/min) when Paraformaldehyde Solutions (3.6% HCHO) were used to generate test atmospheres.
- Measured Diffusive Sampling Rates were somewhat higher (+13% on average) when Formalin Solutions (3.6% HCHO) were used in place of Paraformaldehyde Solution to generate test atmospheres.
 - For experiments of 3-4 hours duration, measured Sampling Rates were elevated by 4% when Formalin Solutions were used in place of Paraformaldehyde Solutions to generate test atmospheres.
 - For experiments of 1 hour in duration, measured Sampling Rates were elevated by 21% when Formalin Solutions were used in place of Paraformaldehyde Solutions to generate test atmospheres.

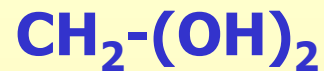
Discussion & Conclusions

- It has been reported by OSHA that measured Diffusive Sampling Rates may be lower than normal when Formalin solutions are the source of formaldehyde exposure.
 - In practice, this would lead to under-estimated exposures when Diffusive Samplers are used in environments where the source of exposure is Formalin.
- Based on this study, Sampling Rates have been found to be slightly elevated (ave. +13%) when Formalin solutions were the source of formaldehyde exposure.
 - In practice, this would result in over-estimated exposures when Diffusive Samplers are used in environments where the source of exposure is Formalin.
- Since two studies contradict each, and neither has included all the environmental conditions occurring in the real-world, additional studies will be needed to completely elucidate the situation.

Composition of Vapors Generated using Paraformaldehyde Solutions

(other than pure anhydrous formaldehyde)

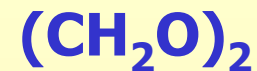
It is likely that evaporation of paraformaldehyde solution
may generate formaldehyde vapor species in addition to
 CH_2O



Formaldehyde Hydrate

Methylene Glycol

MW = 48.0



Formaldehyde Dimer

MW = 60.0