

Technical Report

Description of Possible Sampling Error with AT571 Sampler in Certain Environments where Formaldehyde Exposure Arises from Formalin

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Date: 10-12-2009

Background

OSHA Method 1007 describes a procedure using the AT571 Sampler for sampling formaldehyde in workplace air, and includes data generated in OSHA's method evaluation and approval. Overall, OSHA 1007 finds the AT571 Sampler an acceptable sampling method both for PELs and STELs.

OSHA Concerns

In the same document, *OSHA warns of possible sampling error in environments where the source of formaldehyde exposure is formalin*. As OSHA explains, the methanol present in formalin solutions tends to form a complex with formaldehyde. In solution, this formaldehyde-methanol complex exists in equilibrium with formaldehyde hydrate (the complex between formaldehyde and water). To the extent that some of the complex evaporates from the formalin and persists in the worker's breathing air, a diffusive sampler may underestimate exposures due to the formaldehyde-methanol complex (a larger molecule) having a lower diffusive sampling rate than that of "free" formaldehyde.

Origins in Swedish Publication

This idea was originally posed as a hypothetical problem in a Swedish publication (I. Pengelly et al., Ann. Occup. Hyg., Vol. 40, No. 5, pp 555-567, 1996) in which the investigators suggested *the theoretical possibility that under-sampling error as great as 35% might occur with diffusive sampling if the vapors arising from formalin solution were predominantly methoxymethanol (the name of the complex) with no free formaldehyde*.

Side-by-Side Studies

As a practical matter, the Swedish investigators and OSHA both admit that there is a tendency of methoxymethanol to revert to free formaldehyde in water or moist air. Thus, it is an open question whether, in a particular environment, enough methoxymethanol is actually present to cause significant error. In the Swedish study, formalin environments in the field were studied side-by-side with pump-and-tube versus diffusive samplers. In one study, the results were identical. In the second study, the diffusive samplers were lower by 10%.

Assay Technology performed studies (AIHce 2007) in which pump-and-tube samplers were compared with diffusive samplers using dilute formalin (3.7% formaldehyde, 1.5% methanol). In these studies, diffusive samplers actually gave slightly higher results than pump-and-tube samplers.

Error Linked to Methanol Content of Formalin

Significantly, in OSHA's lab-only studies from the Method 1007 report (Table 1, below), the amount of under-sampling error was studied as a function of the methanol concentration of the formalin solution (the idea being that higher methanol concentration in the formalin would lead to more methoxymethanol and more sampling error.) OSHA's studies were admittedly "worst case" in that vapors were sampled as they emerged from heated formalin without giving methoxymethanol vapor any time to "age" and revert back to free formaldehyde.

Following, in Table 1, are the OSHA data as they appear in OSHA Method 1007. The numbers in the Table consist of the % *Recovery* observed when formalin vapor of stated methanol content is used as a source of formaldehyde vapor.

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These data show a trend of higher recovery (lower error) as the methanol content of formalin decreases.

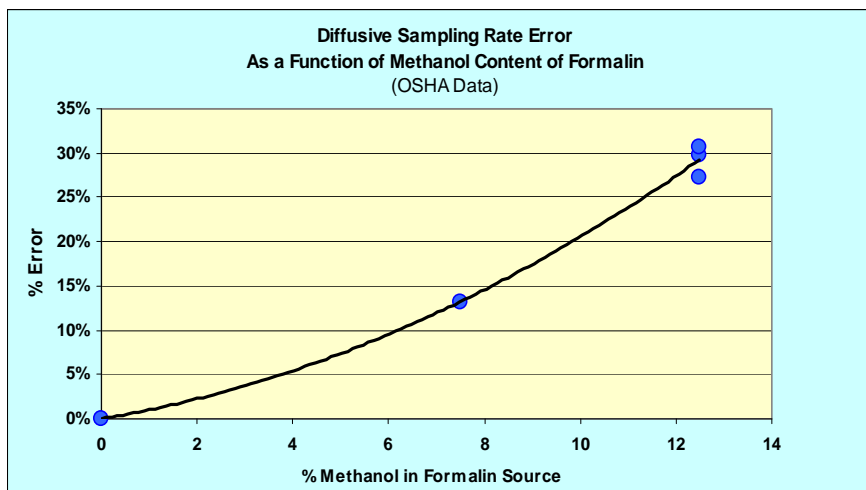
Table 1 (Table 4.9.4 from OSHA 1007)
Methyl Alcohol in the Formaldehyde Solution Effect on Recovery

Source (% methyl alcohol)	% of theoretical for ChemDisk-AL				% of theoretical for UMEx 100				% of theoretical for DSD-DNPH			
	1	2	3	mean	1	2	3	mean	1	2	3	mean
Aldrich (7-8)	85.5	87.1	87.7	86.8	85.5	87.4	86.9	86.6	85.6	87.3	86.2	86.4
Aldrich (10-15)	71.7	73.9	72.6	72.7	72.5	69.3	70.9	70.9	72.2	70.6	71.8	71.5
Aldrich (10-15)	71.6	70.9	68.1	70.2	70.8	71.9	69.3	70.7	71.9	68.4	70.8	70.3
Sigm (10-15)	70.4	69.7	67.9	69.3	68.6	69.6	67.8	68.7	70.5	68.6	67.8	69.0

We took OSHA's data from Table 1 and calculated the "% Sampling Error" by Subtracting the % Recovery from 100%. This Table and the Graph (below) makes the trend easy to observe.

Table 2
Effect of Methanol Content of Formalin on Sampling Error

Formaldehyde Source	% MeOH (w/w)	Ave % Recovery	Ave % Error
Paraformaldehyde	0.0	100.0%	0.0%
Aldrich Formalin A	7.5	86.8%	13.2%
Aldrich Formalin B	12.5	72.7%	27.3%
Aldrich Formalin C	12.5	70.2%	29.8%
Sigma Formalin	12.5	69.3%	30.7%



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Conclusion

The graph (above) suggests persuasively that, in the "worst case", *the Sampling Error due to Diffusive Sampling should be less than 3% if the methanol content of formalin is less than 3% methanol.*

As it happens, the most common formalin solution in use by pathologists, commonly known as "dilute formalin" or "10% Formalin" consists of 3-4% formaldehyde and 1.0-1.5% methanol. This mixture is a 1:10 dilution of the common formalin produced in chemical plants which consists of 37% formalin with 10-15% methanol. Although OSHA used the un-diluted formalin in its studies, the formalin most commonly used in hospitals has 1/10 the content of methanol as that used in the OSHA study.

For the above reasons, **we believe the sampling error arising from using formalin as a source of formaldehyde when sampling with the AT571 Sampler (or any diffusive sampler) will be minimal so long as the methanol content of the formalin solution in use is less than or equal to 3% methanol.** Employers using formalin have the ability to contact their suppliers and obtain the methanol content of formalin they wish to use. In many cases, the methanol content of formalin is listed in the MSDS provided by the supplier.