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Technical Bulletin

June, 2021

# Laboratory Validation of 3M™ Formaldehyde Monitor 3720+, 3721+

## These tests for the evaluation of diffusive air samplers were conducted within the guidelines described in ANSI 104-1998.

The 3M™ Formaldehyde Monitor 3721+ and 3720+ (with prepaid analysis) consist of a fiberglass wafer treated with 2,4-dinitrophenylhydrazine (DNPH) encased within a 76-port polypropylene sampling grid and contained within a polypropylene sampler body.

The use of 2,4-DNPH for derivatization of aldehydes has been documented in air sampling (*e.g.* G. Andersson, K. Andersson, C.-A. Nilsson, J.-O. Levin, *Chemosphere, 1979, 8* (10)*,* 823-827*;* J.-O. Levin, K. Andersson, R. Lindahl, C.-A. Nilsson, *Anal. Chem.*,1985, *57*(6), 1032-1035) and analysis of DNPH-aldehyde derivatives can be performed via HPLC (e.g. EPA Method TO-11, OSHA Method 64).

The 3720+/3721+ can be used for monitoring the following aldehydes:

- Formaldehyde
- Glutaraldehyde
- *o*-Phthalaldehyde (OPA, cannot sample concurrently with other aldehydes)
- Acetaldehyde

Additional external testing on this product was conducted in 2004 by the Occupational Safety and Health Administration (OSHA) Methods Development Team and can be found online.

https://www.osha.gov/dts/sltc/methods/studies/srvassay/srvassay.html

## 1. Test Apparatus & Method

The method for generating challenge chambers for testing samplers is as follows:

Vapor exposures were created by dynamic dilution from a liquid phase containing aldehydes in solution. The liquid analyte mixture was injected into a flowing stream of air at a fixed rate via a syringe pump (Harvard), and was then dynamically mixed with flow-controlled input air provided by the Miller-Nelson 501 atmosphere conditioner. The controlled mixture was passed through an inert acrylic chamber containing diffusive samplers under test. Flows were verified by calibration. Air samples were drawn continuously from the vicinity of the samplers and conveyed to external twin impingers which were subsequently analyzed for formaldehyde via NIOSH 3500 (chromotropic acid method).

Similar methodology was employed by the Wisconsin Occupational Health Laboratory in its independent study for which results are also included in this report.

## 2. Desorption Efficiency (DE)

Analyte recovery and desorption efficiency were determined by analysis of diffusive samplers spiked from standard analyte solutions. A DNPH-impregnated wafer was spiked with a known quantity of aldehyde using a microsyringe, and was placed into a glass vial which was sealed. After equilibration, a measured volume of solvent (acetonitrile) was added. A control containing an identical quantity of analyte in acetonitrile was treated in a parallel manner.

Desorption efficiencies of 100% were found in all studies, as the DNPH derivative as no affinity for the fiberglass wafer.

## 3. Determination of the Effect of Concentration and Time on Sampling Rate (verification of diffusive sampling rate)

Formaldehyde levels ranging from 0.1 to 13 ppm with exposure times ranging from 15 min to 24 hours were monitored with all values in four separate studies clustering around a single regression line.

The linear response of the monitor over a wide dynamic range with low background demonstrates dosimetric performance capable of effectively monitoring 15-minutes STELs (0.2-5ppm) (Figure 1), 8-hr TWAs (0.01-3ppm), or 24-hr Indoor Air Quality tests (below 0.01 ppm).

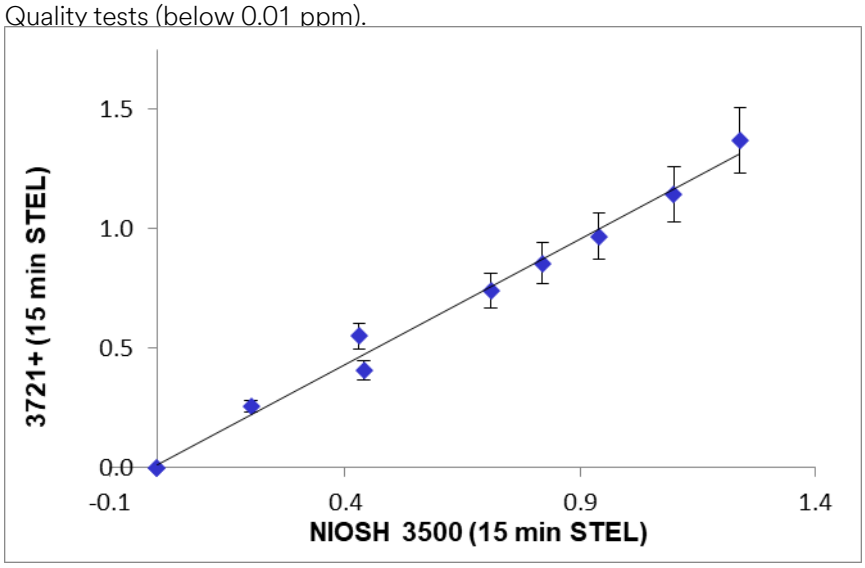


**Figure 1**. 3721+ sampler vs NIOSH 3500 (15 min STEL)

The sampling rate was determined from least squares linear regression analysis of the data. The slope of the plot of formaldehyde exposure in ppm-hr (referenced to the NIOSH 3500 Method) versus formaldehyde found (µg) in the sampler yielded the sampling rate when the slope was multiplied by the molar volume, divided by the molecular weight, and appropriate unit conversion factors were applied.

A formal sampling rate value was taken from data of studies performed in 1993 representing the manufacturing and analytical methodology. The samplers were also evaluated by Wisconsin Occupational Health Laboratory (WOHL; Madison, Wisconsin). When several rounds of testing were compared, no significant differences were observed indicating that the sampling rate is stable with respect to manufacturing variables (Figures 2-4).

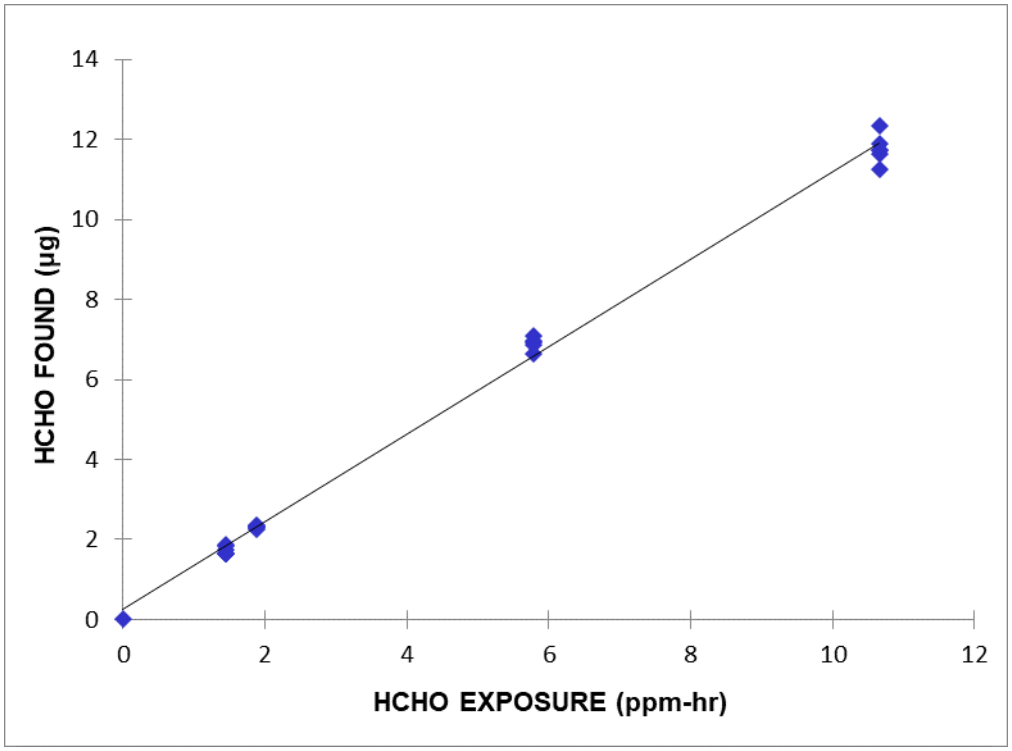


**Figure 2**. Mass collected vs formaldehyde level (Sep 93)

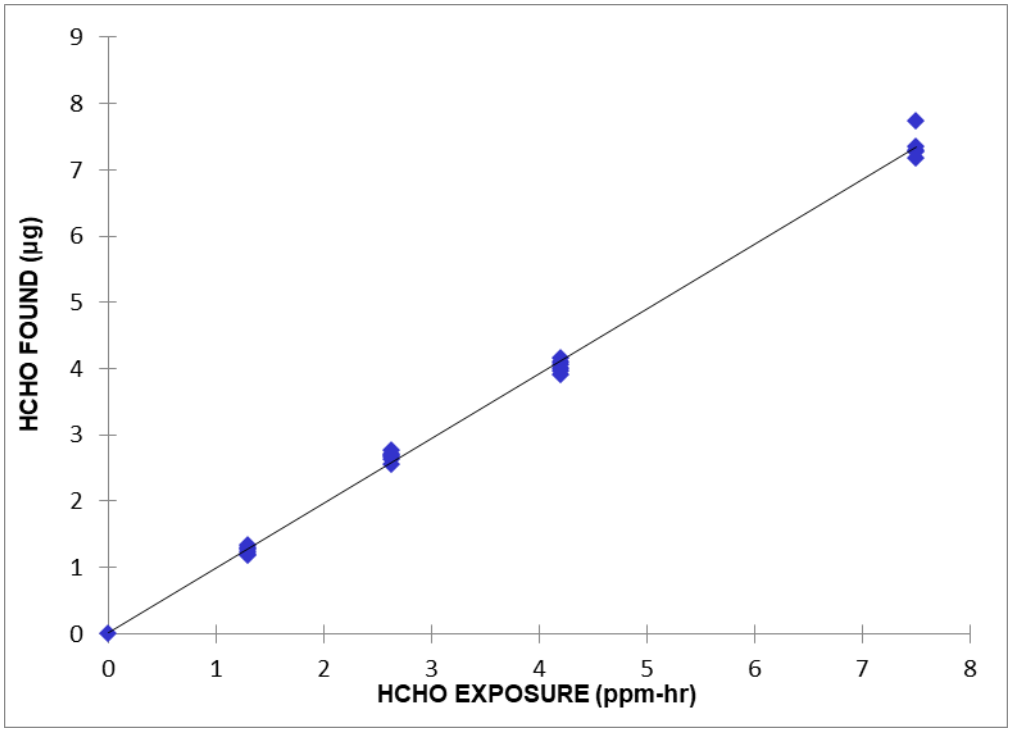


**Figure 3**. Mass collected vs formaldehyde level (July 93)

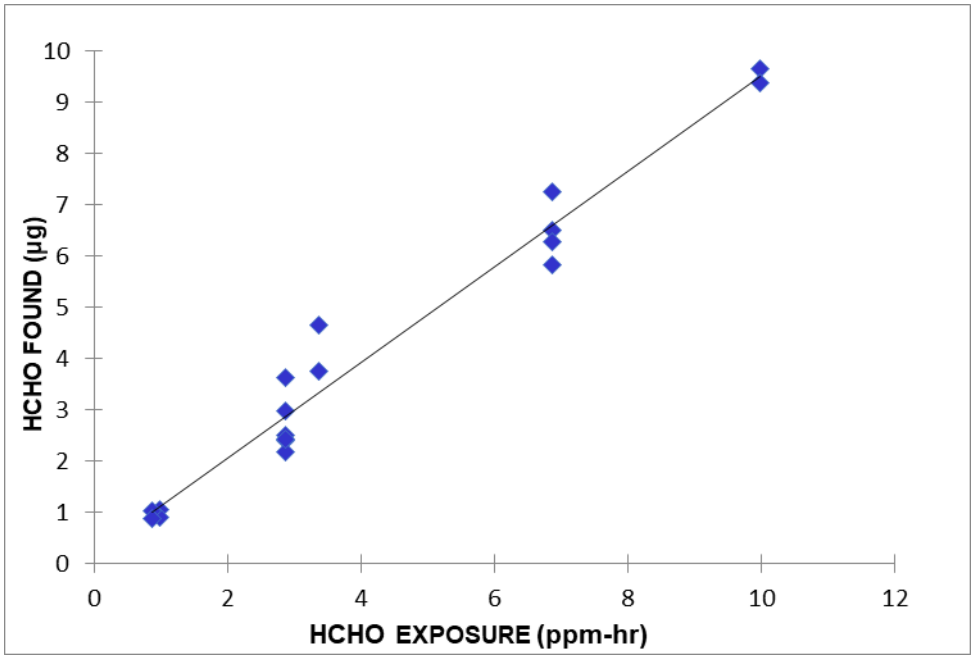


**Figure 4**. Mass collected vs formaldehyde level (WOHL study)

## 4. Background (Blank) Determination

Ultimate sensitivity in an analytical system is a product of the quantity of sample collected and the inherent sensitivity of the analytical method used. The high sensitivity of the HPLC analysis with UV-visible detector in the vicinity of 355 nm balances the moderate sampling rates available with diffusive samplers and, overall, provides a method capable of detecting less than 0.1 ppm-hr of most aldehydes.

Since formaldehyde is ubiquitous in the environment, every laboratory has experienced problems with high formaldehyde blanks arising from the presence of formaldehyde in air, water, building materials, paper, plastics shampoo, etc. Accordingly, each material in contact with product inside the hermetically-sealed pouch (including the pouch itself) has been tested for its contribution to the background blank. In addition, key components are heat-treated during manufacture to further minimize any accumulation of aldehydes.

The reagent-treated wafer on which formaldehyde is collected has been prepared from an inert fiberglass shown to be superior to paper with respect to both its inertness and its lower formaldehyde content. To minimize formaldehyde and enhance shelf life, the process of treating and packaging the wafers has been designed to be carried out entirely in an environment of nitrogen which serves to minimize pickup of ambient formaldehyde and to preserve the reagent system from oxidation.

## 5. Atmospheric Effects

Air Velocity & Orientation – Previous studies demonstrated that there is no significant effect of air velocity and orientation on sampling rate.

Temperature and Humidity – Previous studies demonstrated the absence of an effect of temperature and humidity on sampling rate in the range 0-50°C and 20-80% RH.

## 6. Reverse Diffusion

In order to confirm that sample collected is not lost during the sampling period, a reverse diffusion experiment is conducted. In this test, samplers are exposed at a level equivalent to exposure at the PEL for eight hours, then allowed to stand under ambient conditions (as if sampling) in an environment containing no analyte.

If the practical sampling capacity is exceeded or the derivative to analyze is unstable, reverse diffusion effects would be detected as a loss of analyte when the quantity of analyte recovered from a reverse diffusion sample compared to the quantity recovered by a control sample.

In order to consider there to be no reverse diffusion, the quantity of analyte recovered from the challenge samples exposed at the PEL must be at least 90% or greater of the quantity recovered from control samples.

In the case of 3721+ samplers, those challenged with one day of post-exposure standing in open air (zero formaldehyde level) met the requirements of this test and showed negligible loss of formaldehyde.

## 7. Analyte Stability (storage post-sampling)

A challenge test to assess the stability of the collected analyte on the media after sampling was conducted by exposing a set of samplers to a high level and low level formaldehyde concentration in two separate chamber studies. Samplers were divided for analysis at several time periods: intitial recovery and 1-, 2-, and 3-week recovery. Table 1 and Figure 5 summarize these results.

**Table 1.** Stability of formaldehyde on 3721+; average quantity recovered and % of initial collection.

| **Formaldehyde Low Level (3 µg nominal challenge)** | | |
|---|---|---|
| Holding Time | Avg Qty (µg) | % Recovery |
| Initial | 3.9 | 100% |
| 1 week | 3.5 | 90% |
| 2 weeks | 3.6 | 92% |
| 3 weeks | 3.2 | 82% |
| | | |
| **Formaldehyde Low Level (10 µg nominal challenge)** | | |
| Holding Time | Avg Qty (µg) | % Recovery |
| Initial | 10.1 | 100% |
| 1 week | 10.9 | 108% |
| 2 weeks | 9.9 | 98% |
| 3 weeks | 8.6 | 85% |

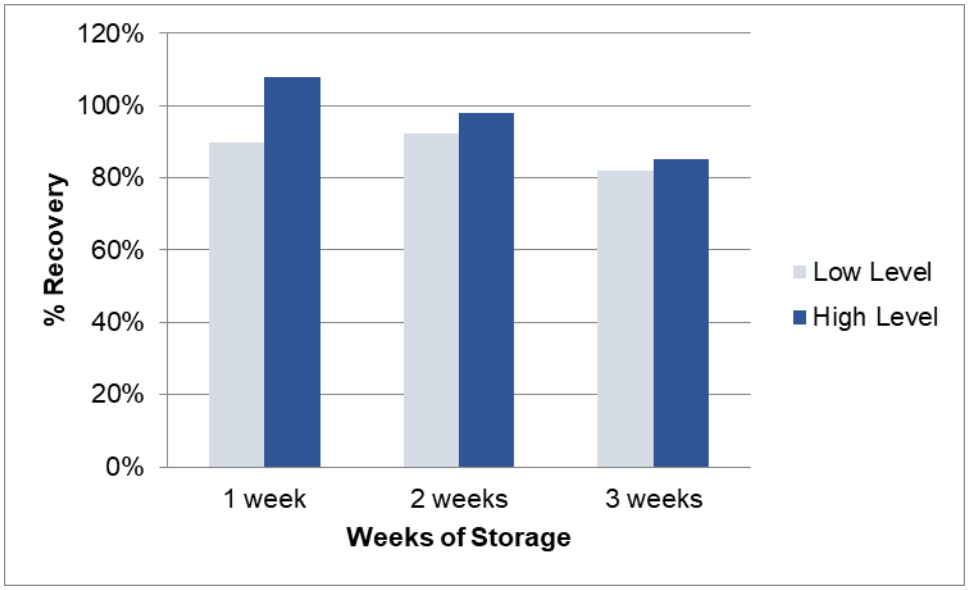


**Figure 5.**Formaldehyde stability on 3721+

## 8. Capacity

Sample capacity is determined largely by the quantity of DNPH on the wafer for reaction with aldehyde vapors. The wafers are each treated with a quantity of DNPH reagent which is capable of reacting with more than 3 µmoles of aldehyde (e.g. equivalent to more than 100 µg of formaldehyde). Taking the sampling rate for formaldehyde into account, the 3721+ has the capacity to sample a formaldehyde exposure in excess of 80 ppm-hour (equivalent to 10 ppm for an 8-hr sampling time). A linear relationship between the formaldehyde exposure level (ppm) and formaldehyde collected (µg)has been shown for formaldehyde levels in the range of 0.1-30 ppm-hr.

## 9. Summary Comments

Sampler 3721+ has been evaluated, and is recommended for sampling aldehyde vapor under the following conditions.

| | |
|---|---|
| Concentrating Range | 0.2 - 2.0 times the OEL |
| Sampling Time | 15 min - 8 hr |
| Air Velocity | 15 - 150 cm/sec |
| Temperature | 0 - 50°C |
| Humidity | 20 - 80% RH |

For maximum shelf life, the product should be stored under refrigerated conditions, but does *not* need to be stored under refrigerated conditions after sampling.

The recommended maximum holding time after sampling is 28 days at room temperature.

It is recommended that Sampler 3721+ be used within the envelope of conditions specified above, but, in general, minor excursions outside these limits would be expected to have only minor effects. Longer or shorter sampling times are possible but have not been evaluated here.

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