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Simple and Convenient Formaldehyde Testing Using Thermal Desorption Tubes

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Formaldehyde exposure is difficult for people to avoid since formaldehyde is present naturally in the environment in variable amounts ranging from less than 1 ng/L in remote areas to 10-20 ng/L in urban environments [1]. Indoor levels are elevated due to off-gassing of formaldehyde from materials of construction (MOC) and is further exacerbated by improvements in energy efficiency in building construction, which leads to the unintended consequence of more efficient indoor trapping of VOCs and formaldehyde. The objective of this paper is to provide a general guide for understanding formaldehyde sources and formaldehyde testing. A secondary objective is to provide an overview of the impact of formaldehyde on indoor air quality.

Previously, Technical Bulletin TB536 provided an overview of formaldehyde and formaldehyde testing at Prism [2]. Formaldehyde exposure can have serious health consequences, especially for asthmatics and individuals that suffer from multiple chemical sensitivities (MCS). Exposure to formaldehyde can lead to respiratory distress, eye irritation, and other symptoms [3]. For individuals with MCS, these symptoms can occur at room concentrations of 100 ppb or lower. The International Agency for Research on Cancer (IARC) reclassified formaldehyde from “probably carcinogenic to humans” to “carcinogenic to humans” in 2004 [4].

Formaldehyde air testing has traditionally required the inconvenience of placing 2,4-dinitrophenylhydrazine (DNPH) sampling tubes into cold storage for immediate shipping to a laboratory. Prism Analytical Technologies has developed a formaldehyde method based on fluorescence technology that offers a simple, convenient, and accurate formaldehyde air test using thermal desorption tubes (TDT). Immediate shipping under cold storage is not required using Prism’s method.

Formaldehyde Sources

Formaldehyde has many sources. Natural wood, which contains cellulose, is a source of formaldehyde. Engineered hardwood and bamboo laminate flooring, cabinetry, plywood, oriented strand board (OSB), and older insulation made from urea formaldehyde and phenol formaldehyde can all be significant sources of formaldehyde. Adhesives and liquid nail products can contain a significant amount of formaldehyde, which is emitted during application and curing of the adhesive. Formaldehyde is also a product from incomplete combustion such as from natural gas, from fireplaces, and from tobacco smoke. Knowledge of the sources of formaldehyde and the use of proper measurement techniques are a necessity for understanding indoor air formaldehyde levels.

Enhanced Public Awareness of Formaldehyde Exposure Risks

Formaldehyde exposure risks recently came to the front of public awareness following a 2015 CBS 60 Minutes episode describing elevated formaldehyde levels from composite wood flooring manufactured in China [5]. This issue led to general confusion and concern for home and business owners who had laminate flooring installed in their buildings. Many clients wanted to test their laminate flooring directly believing that could help them to assess the severity of formaldehyde exposure. What was actually more important was the size of the room that the flooring was installed in and the ventilation available in this room. Formaldehyde concerns were heightened for all consumers who used similar products.

Looking back, this issue was complicated by the difference between product compliance testing, such as the CARB-2 method discussed below and referenced in the 60 Minutes episode, and the emissions from the finished products. Compliance testing is typically performed under specific conditions and applies to components of the product, not the final fully-assembled product. As such, it is almost impossible to replicate the compliance testing conditions once the material is installed in a residential or commercial building. However, since the installed product was all most people had to test, the question of which technique and conditions would give the most representative results became critical: passive (i.e., badge monitoring) vs active (i.e., pumped sampling); room sampling vs product off-gas sampling.

There are many ways that products are tested for compliance. For instance, large-scale chamber testing (i.e., CARB-2 testing) is used for determination of formaldehyde emissions from specific MOC [6]. The California Air Resource Board (CARB) has developed stringent methods for determining formaldehyde levels from various wood materials, usually with the intent of demonstrating that a material is “compliant” with allowable formaldehyde levels. Typically, this type of testing is employed by product manufacturers who need to verify their products are compliant with allowable formaldehyde emissions.

Compliance testing simply determines whether a product meets a certain set of pre-established parameters so that it can be sold with approval from the sanctioning organization. What is more important from the consumer's perspective is what is the actual level of formaldehyde present in their "breathing zone". This can be measured using passive or active sampling.

Passive vs. Active Sampling

Passive room sampling relies on diffusion of formaldehyde into a sampling device such as a badge. The badge typically needs to be in place at least 24 hours to get a valid reading. Passive sampling results typically have greater uncertainty because variations in air flow and environmental conditions can cause changes in the diffusion rate [8]. Active sampling, such as Prism uses, for determining formaldehyde concentration controls the air flow with a calibrated sampling pump which results in a more accurate sample volume.

Room Testing vs. Off-Gas Testing

Active sampling using a TDT provides a "snap-shot" in time of formaldehyde present that occupants are exposed to under ambient conditions. The "snap-shot" is a composite result of formaldehyde from multiple sources. In comparison, off-gas testing measures the amount of formaldehyde emitted from a specific material under controlled conditions and is not representative of what an occupant will experience under ambient living conditions. Off-gas testing can be useful for comparing the amount of formaldehyde emitted from various MOC under identical testing conditions.

Though room formaldehyde levels depend on off-gassing from available sources, equally important for controlling formaldehyde levels in indoor air is proper ventilation, temperature, and humidity controls. Formaldehyde levels are magnified with increased temperature, increased humidity, and poor ventilation. Therefore, "acceptable" concentrations of formaldehyde can exist in locations where CARB-2 non-compliant materials are used. Conversely, concentrations may be elevated in areas where all MOC are compliant, but humidity and/or ventilation may be insufficient.

When formaldehyde levels are elevated in indoor air, source reduction, ventilation modification, or some other remediation method should be employed to reduce the formaldehyde levels. These areas should be addressed before consumers make the expensive decision of removing MOC. One must keep in mind that removal of materials and replacement with other materials can lead to other immediate formaldehyde problems.

Recently, ozonation and other remediation techniques involving energetic radiation have been employed to try to reduce formaldehyde levels in indoor air. Caution must be taken when using these techniques because they frequently lead to additional problems. For instance, ozonation can damage MOC, especially rubber and plastic, and has been known to generate additional by-products, including formaldehyde, which is counter-productive to the remediation effort [10].

Analysis Techniques: Prism TDT Hantzsch Method vs. Silica gel tube DNPH method

Different methods exist for formaldehyde testing. One of the common methods uses a silica gel tube treated with 2,4-dinitrophenylhydrazine (DNPH), where the formaldehyde is derivatized (chemically converted) in the tube to a stable derivative that is subsequently analyzed using HPLC (high pressure liquid chromatography). This method, outlined in EPA Method TO-11A, NIOSH 2016, and ISO 16000-3 [9], requires that the tube be chilled before and after sampling as well as during shipping because the derivative is unstable at room temperature. Several other compounds that contain a carbonyl group (e.g., aldehydes and ketones) in the air sample are derivatized also, so these interferences require separation by HPLC to determine the concentration of formaldehyde.

The Prism TDT Method uses a fluorescence measurement technique to detect the highly specific reaction product of formaldehyde with 2,4-pentanedione and ammonia. This derivatization reaction occurs *in-situ* in the instrument thereby eliminating the need to chill the TDT during shipping. The *in-situ* reaction produces 3,5-diacetyl-1,4-dihydrotoluidine (DDL), which absorbs light at 410 nanometers (nm) and shows strong fluorescence at 510 nm. The fluorescence is detected using an AL 4021 Aero Laser Fluorimeter.

Prism and DNPH Formaldehyde Testing Comparison

Prism recently completed comparison testing of our TDT formaldehyde method with the silica gel tube DNPH method. The comparison included analyzing Laboratory Control Spikes (LCS) and replicate air samples using both methods. The DNPH samples were analyzed by an independent AIHA accredited laboratory.

Results for the LCS spanning a typical formaldehyde concentration range were within ± 10% relative error for both methods. The results for replicate air samples are summarized in the table below. Each of the 5 samples were collected simultaneously in the same location (replicates).

Sample	Volume	Prism TDT	DNPH silica gel tube
Air Sample #1	6.6 L	64 ng/L	
Air Sample #2	5.8 L	62 ng/L	
Air Sample #3	6.6 L	65 ng/L	
Air Sample #4	9.6 L		64 ng/L
Air Sample #5	7.0 L		54 ng/L
Average		63.7 ng/L	59 ng/L
RSD		± 2%	± 8%

RSD – relative standard deviation

These results show an excellent correlation between the two methods. Other procedural comparisons between the two methods are shown here:

	Prism	DNPH
Media	TDT	DNPH silica gel cartridge
Sample Time	20-30 min	Variable; depends on flow rate
Sample flow rate	0.1 -0.2 L/min	0.1 – 2.0 L/min
Shipping	1-2 Day Standard Shipping	Chilled Overnight
Minimum Detectable quantity	60 ng	70 ng [9]

Acceptable Formaldehyde Levels

The National Institute of Occupational Safety and Health (NIOSH) has set a workplace recommended formaldehyde exposure limit (REL) of 20 ng/L (16 ppb) [11]. The Occupational Safety and Health Administration (OSHA) has set a workplace permissible exposure limit (PEL) of 940 ng/L (750 ppb) [12]. Most homes measured by Prism's air test have formaldehyde concentrations in the range of 30 to 70 ng/L (24 to 56 ppb) based on statistical analysis of client data. Various formaldehyde exposure recommendations are summarized in the chart below:

Organization	Concentration ng/L	Concentration ppb	Year Issued	Comments
WHO	100	80	1987	0.5 hour
LEED*	32	27		4 hour
California	94 33 3	76 27 2	1999 2004 2005	1 hour (acute) 8 hour (interim) Annual average (chronic)
Canada	120 50	100 40	2005 2005	1 hour 8 hour
UK	100	80	2004	0.5 hour
Germany	120	100	1977	
France	50 10	40 8	2008	2 hour (proposed) Long-term (proposed)
Norway	100 60	80 50	1999 1990	0.5 hour 24 hour
Australia	100	80	2009	
China	100	80	2003	1 hour
Japan	100	80	1997	0.5 hour
Hong Kong	100 30	81 25	2003	Good Excellent

For those seeking green building certification, the Green Building Council Leadership in Energy & Environmental Design (LEED) has set a limit of 32 ng/L (27 ppb) for uninhabited new buildings [13]. This value remains the same for LEED V4, which took effect for new building projects initiated in November 2016 [14].

The World Health Organization (WHO) recommends that formaldehyde concentrations not exceed 100-120 ng/L (80-100 ppb) for short-term exposure (i.e., 0.5 hour). The WHO has determined average concentrations to be 1-20 ng/L in ambient air and 30 to 60 ng/L for conventional homes and non-occupational workplaces [15]. Few countries list any long-term exposure guidelines. France has a proposed long-term guideline of 10 ng/L (8 ppb), while Norway has a 24-hour exposure limit of 60 ng/L (50 ppb).

Prism has established the following general guidelines for low, moderate, elevated, and high levels of formaldehyde:

Low < 20 ng/L **Moderate** 20-50 ng/L **Elevated** 50-100 ng/L **High** > 100 ng/L

The Low level has been established based on the NIOSH REL and the High level has been established in consideration of the WHO short term exposure guideline. For formaldehyde levels in the Low range, no significant formaldehyde issues exist in the home or building. For Moderate levels, no significant issues exist, but improvement may be achieved by locating and removing the source or adding ventilation. For Elevated levels, it is highly recommended that sources be located and removed and ventilation improvements be made. Finally, for High levels of formaldehyde, occupants may experience respiratory and/or throat discomfort and it is imperative for sources to be located and removed or additional ventilation to be incorporated into the home or building. Note that these exposure estimates apply to healthy individuals, those with significant respiratory conditions or other serious health concerns may experience effects at lower concentrations.

Regardless of these general guidelines, the key for healthy indoor air quality is to minimize formaldehyde and VOC exposure everywhere possible. Every person is unique in their reaction to formaldehyde. Source reduction and ventilation improvements are typically the best ways to reduce exposure in indoor air. Where source reduction isn't possible, an air cleaner equipped with a carbon bed adsorbent can be helpful in reducing indoor formaldehyde levels.

In summary, Prism's TDT fluorescence method for formaldehyde testing provides for quick and simple sampling where the TDTs can be shipped via standard mail and do not need to be stored or shipped in a chilled container. These features, along with the excellent comparison to the DNPH method, make Prism's formaldehyde testing a convenient, affordable, and accurate method for formaldehyde determination. The Prism formaldehyde method is accredited by the American Industrial Hygiene Association (AIHA).

References

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