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Standard Guide for Measurement Techniques for Formaldehyde in Air¹

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1. Scope

1.1 This guide describes analytical methods for determining formaldehyde concentrations in air.

1.2 The guide is primarily focused on formaldehyde measurement technologies applicable to indoor (including in vehicle and workplace) air and associated environments (that is, chambers or bags, or both, used for formaldehyde emission testing). The described technologies may be applicable to other environments (ambient outdoor).

1.3 This guide reviews a range of commercially available technologies that can be used to measure indoor air formaldehyde concentrations. These technologies typically can measure airborne formaldehyde concentrations with detection limits in the range of 0.04 ppb_v (0.05 $\mu\text{g m}^{-3}$) to 10 ppb_v (12 $\mu\text{g m}^{-3}$). The described technologies are typically applied to research or regulatory applications and not consumer level uses.

1.4 This guide describes the principles behind each method and their advantages and limitations.

1.5 This guide does not attempt to differentiate between the effectiveness of the methods nor determine equivalence of the methods.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This guide is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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2. Referenced Documents

2.1 ASTM Standards:²

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D5197 Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)

D6007 Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber

E1333 Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber

2.2 Other Standards:

ISO 16000-3:2011 Part 3: Determination of formaldehyde and other carbonyl compounds in indoor air and test chamber air — Active sampling method³

40 CFR § 136.6 Method modifications and analytical requirements⁴

3. Terminology

3.1 *Definitions*—For definitions and terms used in this guide, refer to Terminology D1356.

4. Summary of the Guide

4.1 This guide reviews technologies that can be used to determine formaldehyde concentrations in indoor air. Historically, ASTM methods for determining indoor formaldehyde concentrations have been based upon the chromotropic acid method (Test Methods E1333 and D6007) and derivatization using 2,4-Dinitrophenylhydrazine (Test Method D5197). However, alternative technologies have been developed to determine formaldehyde concentrations since these methods obtained consensus approval. These technologies can be time averaging methods or real-time methods. Some involve

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

⁴ Available from U.S. Government Publishing Office (GPO), 732 N. Capitol St., NW, Washington, DC 20401, <http://www.gpo.gov>.

the use of wet chemicals for reactions or extractions. Other methods rely on formaldehyde molecular response to differing energy inputs. The purpose of this guide is to examine the range of methods that can be used and describe the advantages and limitations of each method.

5. Significance and Use

5.1 The objective of this guide is to provide the user with an information base on commercially available instruments and technologies that can be used to measure indoor air formaldehyde concentrations.

5.2 This guide is intended as a repository for formaldehyde measurement technologies that other approved ASTM methods can reference to meet ASTM indoor air formaldehyde quantification needs.

5.3 This guide does not discuss the equivalency of the technologies presented. Each technology may have positive or negative interferences that are unique to that technology. When using a new method, equivalence with old methods should be demonstrated for each matrix, measuring environment and media (that is, each type of wood for formaldehyde emission testing in chamber environments). This is especially true when the method is intended to generate regulatory compliance data. Demonstrating equivalence or compliance, or both, is beyond the scope of this method. For guidance equivalence see

references such as 40 CFR § 136.6 and CEN Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods (1).⁵

6. Formaldehyde Quantification Methods

6.1 There are a wide variety of commercial products that measure formaldehyde in indoor air. The methods vary in sampling time, flow rates, applicable concentration range and sensitivity (Table 1). Not all instruments that use a particular technology will be able to achieve the levels described in Table 1.

6.2 Methods with sampling times of an hour or more are typically referred to as time-averaged methods. These techniques use a sampling pump to pull a known amount of air over a sampling time of an hour or more through an impinger, derivatization cartridge, sorption tube or into a canister. Methods with sample times of less than a minute are typically referred to as real time, semi-real time or online methods. These methods continuously draw air into an instrument. The response of the instrument varies depending on the technology. Sensitivity and sampling flows can vary for each manufacture. Values listed in Table 1 are typical values for the method.

⁵ The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE 1 Typical Parameters for Formaldehyde Measurement Methods Listed in Order of Minimum Sampling Time

| Method | Sampling Flow | Minimum Sampling Time | Detection Limit at Minimum Sampling Time | Typical Sampling Time | Detection Limit at Typical Sampling Time | Reference |
|---|---------------------------|-----------------------|--|-----------------------|---|--------------------------------|
| Chromotropic acid | 1 L/min | 1 h | 10 ppb _v (12 µg m ⁻³) | 1 h | 10 ppb _v (12 µg m ⁻³) | Test Method E1333 ^A |
| Derivatization (DNPH, 2,4-Dinitrophenylhydrazine) | 1 L/min | 5 min | 24 ppb _v (29 µg m ⁻³) | 1 h | 2 ppb _v (2.4 µg m ⁻³) | Test Method D5197 ^A |
| Derivatization (Hantzsch reaction) | 1 L/min | 1.5 min | 0.1 ppb _v (0.12 µg m ⁻³) | 1.5 min | 0.1 ppb _v (0.12 µg m ⁻³) | Vendor ^B |
| Electrochemical cell | 1 L/min | 1 min | 10 ppb _v (12 µg m ⁻³) | 1 min | 10 ppb _v (12 µg m ⁻³) | Vendor ^B |
| Pre-concentration and thermal desorption | 0.005 L/min to 0.05 L/min | 1 min | 5 ppb _v (6 µg m ⁻³) | 8 min | 0.6 ppb _v (0.7 µg m ⁻³) | Vendor ^B |
| Photoacoustic | 1 L/min | 30 s | 0.8 ppb (1.0 µg m ⁻³) | 1 min | 0.5 ppb (0.6 µg m ⁻³) | Vendor ^B |
| Cavity ringdown | 0.4 L/min | 2 s | 1.2 ppb _v (1.4 µg m ⁻³) | 5 min | 0.3 ppb _v (0.4 µg m ⁻³) | Vendor ^B |
| FTIR spectrometer with optical filter | ≥1 L/min | 2 s | 1.0 ppb (1.2 µg m ⁻³) | 1 min | 0.2 ppb (0.2 µg m ⁻³) | Vendor ^B |
| Chemical ionization mass spectrometer | 0.02 L/min to 0.2 L/min | 0.1 s | 10 ppb _v (12 µg m ⁻³) | 1 min | < 0.1 ppb (< 0.12 µg m ⁻³) | Vendor ^B |
| Laser absorption spectrometer | >0.5 L/min | 1 s | 0.1 ppb _v (0.12 µg m ⁻³) | 10 s | 0.04 ppb _v (0.05 µg m ⁻³) | Vendor ^B |

^A Based on minimum reporting limit for method.

^B Based on vendor reported values.

6.3 Sampling protocols varies between technologies (Table 2). Some technologies require that the analytical instrument be present in the environment being sampled (onsite) or have a direct connection to that environment that could include tubing, manifolds or valves. Onsite systems can be used in both field and lab applications. Onsite collection requires the person doing the sampling possess suitable training to use the instrument. For other methods formaldehyde is derivatized or stored in sampling media or containers which are then shipped to a laboratory for quantification (offsite). Collection of offsite samples can require the use of calibrated pumps or flow controllers. Collection of samples for offsite analysis can be performed by personnel who are not familiar with the analytical technique.

6.4 Methods requiring the handling and storage of strong acids, solvents and other chemicals are typically referred to as wet chemistry methods (Table 2). These methods require collected samples to be reacted with chemicals prior to analyses. Derivatization and wet chemistry methods are time intensive and require consumables (wet chemicals, or cartridges).

6.5 The type of training required varies for each method. For offsite methods, the person in the field can have a different type and level of training than the person operating the analytical equipment.

6.6 Some technologies can simultaneously quantify other substances in addition to formaldehyde (Table 2). Other technologies can be tuned via reaction (electrochemical), frequency (spectrometer, photoacoustic) or other means to analyze for other substances. However, these methods may require additional sensors beyond basic formaldehyde analysis systems. Technologies that are used to quantify multiple chemicals at the same time in addition to formaldehyde are listed as “Yes” in Table 2, methods that can be adapted to quantify other chemicals are listed as “Possible”.

6.7 Some methods have known interferents (aldehydes, alcohols, relative humidity, among others). Methods may also have unknown interferants present in indoor air. Some of the methods are relatively newly applied to analysis of indoor air samples and interferents for these methods are not expected but could be present.

6.8 The remainder of this guide outlines the scientific principles upon which each method is based, required materials and instruments, and the advantages and limitations of each method.

CHROMOTROPIC ACID

6.9 *How It Works*—Air is pulled through an impinger containing 20 mL of sodium bisulfite (NaHSO_3) solution. Chromotropic acid ($\text{C}_{10}\text{H}_6\text{O}_8\text{S}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$) is added to the solution. In theory, two chromotropic acid molecules are bound together by one formaldehyde molecule to form a chemical that results in a red-purple color solution (2). The solution is typically shipped to a laboratory for analysis. Formaldehyde concentrations are quantified with a spectrophotometer measuring absorption in the 570 nm to 580 nm range and using standards made from a 37 % formaldehyde liquid solution. Formaldehyde air concentrations are calculated using the concentration in the solution, the volume of sodium bisulfate and volume of air sampled (EPA TO-11A (3)).

6.10 *Requirements*—Quantifying formaldehyde using chromotropic acid requires the following:

- 6.10.1 Calibrated pump to draw air through the impinger.
- 6.10.2 Each sample requires one impinger containing 1 % NaHSO_3 solution.
- 6.10.3 A 1 % chromotropic acid must be pipetted into the NaHSO_3 solution. This process requires personal protective equipment for safe handling of acids.
- 6.10.4 Glassware, pipettes and test tubes are required to prepare dilutions and process samples.

TABLE 2 Characteristics of Formaldehyde Measurement Methods

| Sections | Method | Analytical Location | Wet Chemistry | Consumables | Training | Other Species Quantifiable |
|-------------|---|---------------------|---------------|-------------|--|----------------------------|
| 6.9 – 6.12 | Chromotropic acid | Offsite | Yes | Yes | Field: Sample Collection Lab: Wet Chemistry | No |
| 6.13 – 6.16 | Derivatization (DNPH, 2,4-Dinitrophenylhydrazine) | Offsite | Yes | Yes | Field: Sample Collection Lab: Liquid Chromatography | Yes |
| 6.17 – 6.20 | Derivatization (Hantzsch reaction) | Onsite | Yes | Yes | Lab: Wet Chemistry | No |
| 6.21 – 6.24 | Electrochemical cell | Onsite | No | Yes | General Instrumentation | Possible |
| 6.25 – 6.28 | Pre-concentration, thermal desorption | Onsite/Offsite | No | Yes | Field: Sample Collection Lab: Gas Chromatography | Yes |
| 6.29 – 6.32 | Photoacoustic | Onsite | No | No | General Instrumentation | Possible |
| 6.33 – 6.36 | Cavity ringdown | Onsite | No | No | General Instrumentation | Yes |
| 6.37 – 6.40 | FTIR spectrometer with optical filter | Onsite | No | No | General Instrumentation | Yes |
| 6.41 – 6.44 | Chemical ionization mass spectrometer | Onsite | No | No | Ion-molecule reactor chemistry | Yes |
| 6.45 – 6.48 | Laser adsorption spectrometer | Onsite | No | No | General Instrumentation | Possible |

6.10.5 The samples are analyzed in a spectrophotometer with a 10 mm or 12 mm path length.

6.10.6 Distilled water is used for blanks. Standard solutions are diluted from purchased 37 % formaldehyde solutions.

6.11 *Advantages*—This method is documented in ASTM standards (Test Methods **D6007** and **E1333**) and has been used as an international reference method ((**2**), ISO 16000-3:2011). Advantages include:

6.11.1 The chromotropic acid method is ideally suited for sampling of steady-state environments (like constant emissions in emission chambers).

6.11.2 The method is simple to use (**2**).

6.12 *Limitations*—Test Method **D5197** summarizes many of the limitations (along with potential remedies) associated with its use.

6.12.1 Known interferences for the chromotropic acid method including oxidizable organics, phenol, ethanol, alcohols, olefins, aromatic hydrocarbons, cyclohexanone. Metatrioxane, paraformaldehyde, and dimethoxymethane can all have positive interferences. Phenols may cause a negative interference.

6.12.2 This method requires handling concentrated acids. This requires the proper training and appropriate personal protective equipment for the sampling personnel to prevent injury.

6.12.3 A consequence of one-hour sampling times is that chromotropic acid cannot capture the dynamic nature of formaldehyde concentrations in indoor environments.

6.12.4 Cost of impingers and analysis of samples typically limits the number of samples collected in an indoor environment.

6.12.5 Creating appropriate dilutions for reagents and standard solutions requires trained personnel.

6.12.6 This method requires the use of acids and liquid standards. These items must be stored and handled in safe manners that require training and an appropriate disposal plan once used or expired.

DERIVATIZATION (DNPH, 2,4-DINITROPHENYLHYDRAZINE)

6.13 *How It Works*—Air is drawn through a sorbent cartridge containing acidified DNPH coated silica for a known amount of time at a measured flow rate. Each formaldehyde molecule reacts with one DNPH molecule to form one 2,4-dinitrophenylhydrazone derivative. The cartridge is then sealed and shipped to a laboratory for analysis. The derivative is then extracted from the cartridge using a known amount of acetonitrile or other solvent. The concentration of 2,4-dinitrophenylhydrazone derivative in the solvent is quantified using a high-performance liquid chromatography (HPLC) or ultra-high-performance liquid chromatography (UHPLC) with a UV detector or diode array detector operating in the 360 nm to 380 nm range. Formaldehyde concentrations are calculated using the derivation concentration in the solvent, the solvent volume and volume of air sampled.

6.14 *Requirements*—Quantifying formaldehyde using DNPH requires the following:

6.14.1 Calibrated pump to draw air through the DNPH cartridge.

6.14.2 In some applications, a potassium iodide (KI) coated tubing or impregnated filters are needed to remove high ozone background prior to the DNPH cartridge.

6.14.3 Each DNPH sample requires one single-use DNPH cartridge. Cartridges are produced by multiple manufacturers.

6.14.4 DNPH cartridges can be extracted via automated or manual means. The extraction process requires solvent and associated glassware, syringes or automation containers.

6.14.5 An automated HPLC or UHPLC is typically used to determine derivation concentrations.

6.14.6 Purchased standard solutions of the derivative are typically used for quantification.

6.15 *Advantages*—This method is documented in ASTM standards (Test Method **D5197**) and has been used to report data to regulatory agencies. Advantages include:

6.15.1 The DNPH method is suited for sampling of steady-state environments (like constant emissions in emission chambers) or for time integrated applications.

6.15.2 Field collection of sorbent cartridges can be performed by staff with minimal training.

6.15.3 There is minimal danger to personnel performing field collection of samples using DNPH cartridges (no hazardous chemicals).

6.16 *Limitations:*

6.16.1 Test Method **D5197** summarizes many of the limitations (along with common remedies) associated with DNPH formaldehyde sampling. These issues include:

6.16.1.1 Interferences from ozone, nitrogen dioxide and nitric oxide.

6.16.1.2 Poor collection efficiencies at relative humidities above 75 % and below 10 %.

6.16.1.3 Derivative contamination or dissociation from sunlight, temperature, and particles.

6.16.2 In addition, other limitations related to the DNPH method include:

6.16.2.1 One-hour or longer sampling times precludes capturing dynamic formaldehyde concentrations in indoor environments.

6.16.2.2 Cost of cartridges and analysis of samples mean that the number of samples in an indoor environment is typically limited by budgetary constraints.

6.16.2.3 Operation and maintenance of an HPLC or UHPLC requires trained personnel.

6.16.2.4 This method requires the use of solvents and liquid standards. These items must be stored and handled in safe manners that require training and an appropriate disposal plan once used or expired.

DERIVATIZATION (HANTZSCH REACTION)

6.17 *How It Works*—Sample air is drawn through a stripper. The stripper contains a counter flowing aqueous stripping solution into which formaldehyde partitions. The sample flow and the flow of the stripping solution are known. The stripping consists of deionized water and a low concentration of H₂SO₄ to prevent interferences from SO₂. The aqueous solution leaving the stripper is continuously mixed with Hantzsch

reagent in a reactor at elevated temperature. Each formaldehyde molecule reacts with one acetone-acetyl (2,4-pentadione) molecule to form one 3,5-diacetyl-1,4-dihydropyridine derivative (DDL). The concentration of DDL in the output of the reactor is quantified by UV-fluorescence at 510 nm, where the fluorescence light is detected with a photomultiplier. The concentration of formaldehyde is calculated from the raw fluorescence signal, the sample gas flow and the flow of the stripping solution. The linear relationship between the raw data and the formaldehyde concentration is obtained with a known formaldehyde solution and a blank.

6.18 *Requirements*—Quantifying formaldehyde by the Hantzsch reaction continuously requires the following:

6.18.1 3.5 L of Hantzsch-reagent and 5 L stripping solution for a week of continuous operation.

6.18.2 A 0.01 Molar formaldehyde standard solution for calibration.

6.18.3 Glassware, balance, pipettes are required for preparation of the solutions.

6.19 *Advantages*—Advantages of the Hantzsch reaction method include:

6.19.1 The collection efficiency is independent of humidity.

6.19.2 The system can be directly calibrated with a liquid standard.

6.19.3 The method can also be applied to liquid samples.

6.19.4 Commercial products automate the process providing continuous measurement.

6.19.5 Required operator training is limited to wet chemistry processes.

6.19.6 Suited for both steady-state testing and dynamic testing when concentration changes happen at time scales greater than 1.5 minutes.

6.19.7 Can be applied either in field automation or discrete sampling systems (for example, chambers, bags, cylinders).

6.20 *Limitations*—Limitations of the Hantzsch reaction method include:

6.20.1 There are known interferences from ozone and hydrogen peroxide.

6.20.2 Reagent and stripping solution must be prepared manually on a frequent basis.

6.20.3 Peristaltic pump tubing must be replaced frequently.

6.20.4 Calibrations are required at least weekly.

6.20.5 If field deployed occupants should be made aware of reagents present.

6.20.6 Due to the time required for the reaction to occur, there is roughly a 5-minute delay between sampling and measurement.

ELECTROCHEMICAL CELL

6.21 *How It Works*—Air passes over an electrochemical sensor. Formaldehyde diffuses through a membrane and enters an electrolyte solution. A formaldehyde electrochemical reaction occurs at one electrode and a balancing reaction occurs at the counter electrode. The electrons moving through the circuit connecting the electrodes produce an electrical signal proportional to the gas concentration.

6.22 *Requirements*—Quantifying formaldehyde by electrochemical analyzers requires the following:

6.22.1 External power source for extended operation.

6.23 *Advantages*—Electrochemical cell analyzers share the following advantages:

6.23.1 No sample cartridges or impingers are needed to collect samples.

6.23.2 Suitable for both steady-state testing and dynamic testing when concentration changes happen at time scales greater than 1 minute.

6.23.3 Required operator training is limited to general instrumentation.

6.24 *Limitations*—Electrochemical cell analyzers can have the following limitations:

6.24.1 The lifetime of an electrochemical cell is dependent upon the total amount of formaldehyde to which it has been exposed.

6.24.2 Electrochemical cells can corrode.

6.24.3 Electrochemical cell analyzers are most suited for field monitoring due to diffusive nature of sampling.

6.24.4 Known interferences at sub 50 ppbv levels include acetaldehyde, chlorine gas, hydrogen sulfide, hydrochloric acid, sulfur dioxide and nitrogen dioxide. Other interferences include acetone, carbon monoxide, ethanol, glutaraldehyde, hydrogen, isopropanol, methanol, methylethylketone, n-butanol, n-propanol, ammonia, nitrous oxide, phenol, and propionaldehyde.

6.24.5 Water vapor is a known interferent that has been shown to prevent accurate indoor formaldehyde measurements at 45 % to 50 % relative humidity (4).

PRE-CONCENTRATION, THERMAL DESORPTION

6.25 *How It Works*—Air samples first pass through a water abstraction device that converts gas phase water to the solid phase and prevents the absorption of formaldehyde. With most of the excess water removed, samples then pass into the multi-sorbent trap of a thermal desorber, held at $-30\text{ }^{\circ}\text{C}$ to $-40\text{ }^{\circ}\text{C}$, where the analytes are quantitatively retained. Some systems use a single sorbent trap and temperatures of $-150\text{ }^{\circ}\text{C}$ to focus the analytes. The trap can be purged with carrier gas in the sampling direction to eliminate oxygen and further reduce water. Finally, gas flow is reversed, and the trap is heated rapidly (up to $200\text{ }^{\circ}\text{C/s}$) to inject the analytes onto the gas chromatograph (GC) column for detection with mass spectrometry (MS).

6.26 *Requirements*—Quantifying formaldehyde using pre-concentration, thermal desorption requires the following:

6.26.1 A thermal desorption system with a water abstraction device coupled to a GC/MS.

6.26.2 Certified gas or liquid formaldehyde standards to calibrate the MS.

6.26.3 External power source and helium carrier gas.

6.26.4 For systems that cool to $-150\text{ }^{\circ}\text{C}$, liquid nitrogen.

6.26.5 A sampling line from the atmosphere of interest to the thermal desorption system.

6.27 *Advantages*—Pre-concentration, thermal desorption methods share the following advantages: