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A permeation-controlled formaldehyde reference source for application in environmental test chambers

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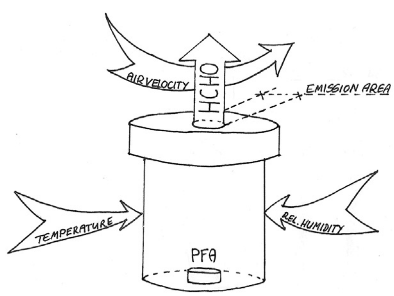
HIGHLIGHTS

- This is the first formaldehyde reference source with realistic emission properties.
- Paraformaldehyde is a suitable polymer for the controlled release of formaldehyde.
- The principle of the reference source is simple and the design is robust.
- The formaldehyde emission rate is stable for more than 20 h.
- The emission behavior of the source can be changed in dependence of temperature and humidity.

GRAPHICAL ABSTRACT



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ABSTRACT

In a wide range of indoor air pollutants, formaldehyde is one of the most-used and best-known substances. In order to protect human health, many countries have established threshold values for the release of formaldehyde from miscellaneous products and revise them constantly. Compliance with these regulations is usually assessed by emission test chamber measurements or derived methods. To control and improve the mechanisms of an emission test chamber, a reliable reference source with sample mimicking emission properties is required but not available so far. This study describes a permeation-controlled reference source based on the application of paraformaldehyde as formaldehyde releasing polymeric compound. Interactions between the formaldehyde release of the source and the governing chamber parameters temperature, relative humidity and air velocity were investigated in 1 m^3 emission chambers. Depending on the conditions, constant formaldehyde concentrations between approximately 10 ppb and 150 ppb can be adjusted for up to 600 h. A linear correlation between the logarithm of the chamber concentration and the reciprocal temperature was found. The results support the feasibility of the source for validation of emission test chamber performance.

1. Introduction

In order to maintain a healthy indoor air quality, permanent regulatory efforts are being made to minimize the release of organic emissions into the indoor environment. Assuring compliance of building products or consumer goods with these regulations requires interference-free emission testing according to

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standardized test protocols (Salthammer, 2014). Generally, so-called emission test chambers are used for this purpose, in which parameters such as temperature, air humidity and air exchange can be precisely adjusted (Salthammer, 2009). In this respect, formaldehyde is one of the well-studied substances, as it has been used industrially for many years and is a constituent of many products (Salthammer et al., 2010).

The International Agency for Research on Cancer (2006) classified formaldehyde as a human carcinogen (Group 1). The European Commission classified it as a 1B carcinogen and mutagen in 2014. In 2010 the WHO confirmed their indoor guideline value for formaldehyde as 0.1 mg/m^3 (World Health Organization, 2010). Wolkoff and Nielsen (2010) investigated the WHO assessment thoroughly and considered an air quality formaldehyde guideline of 0.1 mg/m^3 to be protective against both acute and chronic sensory irritation. The same authors state that the WHO formaldehyde guideline value is also considered defendable for prevention of all types of cancer, including lymphohematopoietic malignancies (Nielsen and Wolkoff, 2010). Over the years, a number of national authorities also reassessed their indoor air guideline values (Salthammer, 2011) and subsequently intend to agree with the WHO recommendation of 0.1 mg/m^3. In 2016, Germany adopted the WHO guideline value (German Committee on Indoor Guide Values, 2016).

As far as the building products sector is concerned, the use of formaldehyde as a component of thermosetting adhesives is of particular significance (Roffael, 1993). Indoor-related applications of formaldehyde in the past and present cover wood-based products (Yrieix et al., 2010), cork products, insulation materials made of urea-formaldehyde foam, mineral wool or glass wool (Gunschera et al., 2013), paper products, coating materials, textiles, cleaning and caring products (Nazaroff and Weschler, 2004), cosmetics (Lefebvre et al., 2012), disinfectants, biocides, preservatives, photo-processing chemicals, etc.

For most indoor products, the emission of formaldehyde is regulated by statutory provisions or voluntary commitments. The US EPA, for example, published “Formaldehyde Emission Standards for Composite Wood Products” in December 2016. In France, a division into emission classes with four ranges from $\leq$10 μg/m^3 to $\geq$120 μg/m^3 and classification from A+ to C has been in existence since 2011. In Germany, the permissible formaldehyde emission from wood-based materials is subject to the Chemikalienverbotsverordnung (Chemicals Prohibition Ordinance). A lowest concentration of interest (LCI) value of 100 μg/m^3 for formaldehyde was proposed by the EU-LCI Working Group within the harmonization framework for the health-based evaluation of indoor emissions from construction products in the European Union (European Collaborative Action, 2013).

The determination of guideline values and limit values requires that emissions from products can be measured with the necessary accuracy and reliability. In addition to the comparatively elaborate test chamber methodology, simplified procedures have therefore been developed specially for wood-based materials (Risholm-Sundman and Wallin, 1999; Risholm-Sundman et al., 2007). Simultaneously, the trend towards ever-lower limit values also leads to higher demands on the analytics. For the determination of formaldehyde in test chambers, it follows that the calibration range below 100 μg/m^3 (approx. 81 ppb) is particularly important for the validation. This in turn presumes the configuration of defined formaldehyde concentrations over hours to days. Formaldehyde is commercially available as a test gas (e.g. 50 ppm in nitrogen). The respectively desired dosage in the chamber is possible (Gunschera et al., 2013), but requires a system with complex apparatus. Moreover, the production of certified test gases is time and cost intensive. Simpler formaldehyde reference sources have therefore been proposed, which possess similar properties to the material samples and which can be positioned in the test chamber.

Initially, polymethylpentane (PMP) films were impinged with toluene and were validated in different chamber studies (Cox et al., 2010; Howard-Reed et al., 2011; Liu et al., 2014). In the case of formaldehyde polycarbonate (PC) films were found to be more suitable (Liu et al., 2013). Production, storage and transport involved, however, a high effort and the release of formaldehyde prior to the actual application of the source could not be prevented. Temperature and relative humidity do not influence the emission behavior; this source can therefore not be deployed for the simulation of real samples.

Wei et al. (2012, 2013; 2014) developed a so-called LIFE source (liquid-inner tube diffusion-film-emission), which was also tested with toluene before the usage for formaldehyde. The LIFE source consists of a Teflon container, whose opening measures 5 mm in diameter and is covered with a film made from polydimethylsiloxane (PDMS), which is intended to ensure a controlled diffusion of the formaldehyde. The source itself is 1 ml of formalin with a concentration of 16%. The emission profile was examined in a 51 l chamber. Constant emission rates were measured over 24 h and extrapolated for a period of over 1000 h. In further experiments, the positive correlation of temperature and emission was determined whilst an influence of the relative humidity could not be established. For VOCs, cured lacquer was also successfully applied as reference material (Schripp et al., 2014; Nohr et al., 2015), but this technique is hardly suitable for formaldehyde.

Until now, there has been no reference source for formaldehyde with controlled emission rates in dependence on temperature and humidity. In this study, a new approach is presented, which is based on the application of paraformaldehyde (PFA) in a steel cylinder as the source of emission and the diffusion of the released formaldehyde through a circular opening of 1–8 mm in diameter.

2. Material and methods

2.1. Design of the reference source

The basis of the reference source discussed here is paraformaldehyde (PFA), as this decomposes into formaldehyde in dependence on temperature and relative humidity (Hori and Arashidani, 1997). The PFA powder (Roth GmbH) is processed into pills, for simpler application. For this purpose, it is initially pestled and 0.5 g are subsequently weighed into a mold. The mold is transferred into a laboratory press (Perkin-Elmer). The PFA is initially compressed by a vacuum over a period of 20 min. Then, 125 bar of hydraulic pressure is additionally applied for 10 min. Following this, the pill is stored in a sealed petri dish at 23 °C and 50% RH.

Direct application of the PFA pills in a 1 m^3 emission test chamber led to rapid and uncontrollable changes in formaldehyde concentration and will not be further discussed in this study. For this reason, a vessel made from stainless steel was developed for the generation of emissions with long-term stability. This vessel consists of a hollow cylinder and an insert with a defined opening, which are connected to one another via a thread (Fig. 1). The thread is sealed using Teflon tape and an O-ring. Via the variable opening of the insert, with diameters (D) of 1–10 mm, it is possible to regulate the emissions.

2.2. Analytics

Formaldehyde (HCHO) was measured with an online analyzer (Aerolaser AL4021) at an air sampling flow rate of 1.0 l/min. The instrument bases on the Hantzsch reaction (acetyl acetone method), which involves the cyclization of 2,4-pentanedione