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On-site calibration system for trace humidity sensors

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ABSTRACT

A portable device for calibration of trace humidity sensors and an adopted calibration procedure have been developed. The calibration device is based on humidity generation by permeating water through polymeric membrane tubes. Water vapour transmission rates for various polymers were experimentally determined in order to select the most suitable polymeric material. The developed trace humidity generator consists of a gas-flow polymeric hose immersed in a water reservoir thermostated by a sensor-controlled heater. Mole fractions of water vapour between 1 μmol mol^{-1} and 350 μmol mol^{-1} (equivalent to frost-point temperatures from −76 °C to −31 °C) were generated by varying either the operating temperature or gas flow. The operating temperature can be varied from 20 °C to 60 °C and kept stable within 0.1 K. Uncertainty analysis indicated that the trace humidity generator produces gas flows of constant humidity amounts with a relative expanded uncertainty less than 3.4% ($k = 2$) of the generated value.

1. Introduction

The measurement of trace humidity in gases in the 1–2000 μmol mol^{-1} concentration range is a significant challenge. Relative uncertainties in the reading less than 1%, typical for temperature and pressure measurements, are difficult to obtain. Trace humidity hygrometers, such as aluminium oxide or polymer-based sensors, are specified for uncertainties in frost point measurement to 7 K. Additionally, such sensors exhibit drift and aging effects after long-term use under industrial working conditions. This entails the demand for recalibration of these sensors at regular time intervals in order to ensure high quality of process gases for application in the pharmaceutical or chemical industries. Two possible approaches for calibrating of trace humidity sensors are applied; comparison with reference gas mixtures of known trace humidity and use of precise reference instruments, such as dew point hygrometers or cavity-ring-down spectrometer (CRDS) [1,2]. These reference methods shall be traceable to the national standards for humidity. In most cases these are extensive facilities of gravimetric, dew-point, diffusion-tube or coulometric trace humidity generators situated in the national metrology institutes (NMI) [3–7]. Calibrations are expensive, because reference instruments are costly and can often be used only in a laboratory.

For producing trace humidity in reference gas mixtures, several methods are available, such as direct injection of liquid water, evaporation of water, or open diffusion tubes [8,9]. The generation based on water vapour permeation through a polymeric tube was implemented in some facilities for calibration of trace humidity sensors to reduce the uncertainty of measurement [10–12]. This method can produce steady-state trace concentrations of water vapour ranging from a few nanograms to some milligrams per normal cubic metre of gas under constant surrounding conditions for a long period of time if an appropriate reservoir of water can be provided. Permeation-based calibration systems for hygrometers measuring trace humidity amounts of less than 1 μmol mol^{-1} in ultra-dry gases were developed e.g. at NIST and PTB [13–16]. A permeation-based system using a 30 m long circular tube of 6 mm outer diameter, filled with air at 50% relative humidity and purged from the outer surface of the tube with dry nitrogen carrier gas was reported by Hudoklin et al. [17].

The objective of this investigation was to elaborate a portable device for on-site calibration of trace humidity sensors in the frost point range of −76 °C to −31 °C, corresponding to water vapour mole fraction in air or other gases from 1 μmol mol^{-1} to 350 μmol mol^{-1}. An operation period of about six months without water refilling was required. Since many trace humidity sensors are exposed to gas streams, the flow of the generated humidified gas should be controlled within the range from 20 L h^{-1} to 300 L h^{-1}. These requests impose requirements concerning the amount of water in the reservoir and the transmission rate of

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water through the polymer tube. Usually, sealed up permeation tubes are used for generation of gas or vapour trace concentrations [11,12]. However, this approach limits long term operation and the supply of large amounts of water vapour into the test gas. A more promising configuration is to let the dry gas flow through a polymer hose immersed in a water reservoir. Assuming a reasonable length of a permeation hose in the range of 0.1–1 m, the water vapour mass flow rate should be in the range of 5–18 μg min^{-1} and the available water reservoir volume shall not be smaller than 0.3 L in order to fulfil the aforementioned requirements.

The permeability of polymers depends on their composition and density, and may differ from one commercial product to another. Therefore, a suitable material had to be selected and long term stability of permeability had to be tested. Many materials have a permeability coefficient strongly dependent on temperature. In many cases a temperature change of 1 K results in a change of transmission rate of about 10%. Thus, a specific temperature needs to be adjusted by using an appropriate heating control of the permeation system.

2. Terminology and theoretical considerations

Permeation is a complex process by which molecules: (1) adsorb onto the material's surface and dissolve in it, (2) diffuse through it because of concentration or partial pressure gradient, and (3) desorb at the other side. Of course, the permeant such as a permanent gas or vapour, the permeated materials – solids or liquids – and the environmental factors have an impact on the course of the permeation process whose description requires numerous assumptions and simplifications. For steady-state permeation of a permanent gas, according to this adsorption–diffusion model, the process can be described by two laws: Henry's law and Fick's first law. The derivative formulation of Fick's first law for one-dimensional diffusion is written as:

$$J = -D \cdot \left(\frac{\partial c}{\partial x}\right) \tag{1}$$

where J is the net flux of permeant (the amount of permeant passing through a unit area of e.g. polymer membrane in unit time), c is the instant value of the permeant concentration for an instant value x of the thickness coordinate, and $\frac{\partial c}{\partial x}$ is the concentration gradient across the membrane thickness. D is the diffusion coefficient (also called diffusivity); the "minus" sign indicates that diffusion of molecules proceeds opposite the concentration gradient. For a homogeneous membrane, after finding the definite integral with the lower limit c_2 – the surface concentration on the "desorption side ($x = \delta$)" of the membrane, and the upper limit c_1 – the surface concentration on the "adsorption side ($x = 0$)" when $c_1 > c_2$, Fick's first law takes the form:

$$J = -D \cdot \left(\frac{\Delta c}{\delta}\right) \tag{2}$$

where $\Delta c = c_1 - c_2$ is the concentration difference, and δ is the membrane thickness. For permanent gases, the flux J is expressed as $J = \frac{\Delta V}{A \cdot \Delta t}$, and reported in cm^3($stp$[1]) m^{-2} s^{-1}. For vapours, the flux J is expressed as $J = \frac{\Delta m}{A \cdot \Delta t}$, and reported in g m^{-2} s^{-1}.

In order to substitute the pressure difference $\Delta p = p_1 - p_2$ (p_1 and p_2 are the partial pressures of the permeant over the membrane sides of the surface concentrations c_1 and c_2, respectively) for Δc, Henry's law can be applied. Henry's law states that the permeant concentration on the membrane surface is directly proportional to the partial pressure of the penetrant over this surface: $c = S \cdot p$, where S is the solubility coefficient (a sorption equilibrium parameter). Permanent gases do obey Henry's law, so the Fick's first law for permanent gases can be rewritten as:

$$J = -D \cdot S \cdot \left(\frac{\Delta p}{\delta}\right) \tag{3}$$

The product of D and S is denoted as P – the permeability coefficient.

The permeation process can be characterised by three parameters.

The first parameter is the transmission rate (TR). For permanent gases it is denoted by the initialism GTR, and for vapours by VTR (for water vapour: $WVTR$, or WVT). In the case of permeation process, TR is a synonym of the flux J. So, for permanent gases TR is reported in cm^3(stp) m^{-2} s^{-1}, and for vapours in g m^{-2} s^{-1} or in g m^{-2} day^{-1}. TR describes the effective amount of the permeant passing through a membrane's unit area in unit time under specified temperature, pressure and humidity conditions. TR depends on both membrane thickness, and its material's properties.

The second parameter is the permeance, Q, which can be calculated as the quotient of TR and the partial pressure difference across the membrane Δp:

$$Q = \frac{J}{\Delta p} = \frac{TR}{\Delta p} \tag{4}$$

The use and calculation of that parameter is limited to the permeants for which Henry's law is valid. These permeants encompass all permanent gases, but for vapours Henry's law is only valid for some materials and some ranges of partial pressures. For permanent gases, the common unit used for permeance is cm^3(stp) m^{-2} s^{-1} Pa^{-1}, and for vapours g m^{-2} s^{-1} Pa^{-1}. The formulae for the permeance (when Henry's law is valid) are:

$$\text{For permanent gases:} \quad Q_G = \frac{J}{\Delta p} = \frac{GTR}{\Delta p} = \frac{\Delta V}{A \cdot \Delta t \cdot \Delta p} \tag{5}$$

$$\text{For vapours (including water vapour):} \quad Q_V = \frac{J}{\Delta p} = \frac{VTR}{\Delta p} = \frac{\Delta m}{A \cdot \Delta t \cdot \Delta p} \tag{6}$$

Permeance is a parameter characterising a certain membrane; it is a performance evaluation, not a property of a material [18].

The third parameter (and the most important one for designers) is the permeability coefficient P (sometimes called for short: permeability). For permeation processes where Henry's law is obeyed, the permeability coefficient P is the arithmetic product of the permeance Q and the thickness δ. So, for permanent gases:

$$P_G = Q_G \cdot \delta = GTR \cdot \frac{\delta}{\Delta p} = \Delta V \cdot \frac{\delta}{A \cdot \Delta t \cdot \Delta p} \tag{7}$$

Both the SI system unit 1 cm^3(stp) mm m^{-2} s^{-1} Pa^{-1} and the CGS system unit 1 Barrer[2] are applied.

For vapours which obey Henry's law for some materials and some ranges of partial pressures (when the permeance can be calculated):

$$P_V = Q_V \cdot \delta = VTR \cdot \frac{\delta}{\Delta p} = \Delta m \cdot \frac{\delta}{A \cdot \Delta t \cdot \Delta p} \tag{8}$$

The unit is g mm m^{-2} s^{-1} Pa^{-1}.

For vapour permeation when the permeance cannot be calculated because Henry's law is not obeyed (e.g. for hydrophilic polymers), a difference of partial pressures cannot be applied to the permeability coefficient calculation. For this case the substitute P' for the permeability coefficient P is reported, for water vapour,

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[1] *stp:* standard conditions of temperature and pressure (273.15 K, 101,325 Pa).

[2] 1 Barrer = 10^{-10} [cm^3(stp)·cm·cm^{-2}·s^{-1}·cmHg^{-1}].