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An unheated permeation device for calibrating atmospheric VOC measurements

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Abstract

The development of an unpowered permeation device for continuous calibration of in-situ instruments measuring atmospheric volatile organic compounds (VOCs) is described. Being lightweight and compact, and containing only negligible amounts of chemicals, the device is especially suited for field use such as onboard aircraft. Its speciality is to maintain the permeation process in thermal equilibrium, i.e. the instantaneous permeation rate can be ascribed via a simple temperature measurement. This equilibrium state is maintained by a combination of three features: (i) a thin PTFE membrane as permeation medium which guarantees short stabilization times, (ii) a water bath as heat buffer, and (iii) a vacuum-panel based insulation, in which features (ii) and (iii) minimize temperature drifts. The uncertainty of the permeation rate due to thermal non-equilibrium is kept below 1%. An extensive theory part details the major permeation processes of gases through porous polymers, being Fick's diffusion, Knudsen flow, and viscous flow. Both the measured stabilization time and the measured temperature dependence of the permeation rate independently indicate that the permeation can be described by a viscous flow model, where diffusion of the gas molecules in large pores (having a diameter of $>0.05\ \mu\text{m}$) dominates.

1 Introduction

Volatile organic compounds (VOCs) such as carbonyls, alcohols, organic nitrates, organic peroxides, and peroxides are extremely relevant for the chemical processing in the atmosphere (Jenkin et al., 1997; Williams, 2004). They inter alia serve as fuel for the photochemical production of ozone (Atkinson, 2000), contribute significantly to the organic components of aerosol particles (Odum et al., 1996, 1997; Jimenez et al., 2009; de Gouw et al., 2011), and produce free radicals influencing the oxidizing capacity of the atmosphere (Singh et al., 1995; Wennberg et al., 1998). However, the quantitative knowledge of their atmospheric budget, i.e. sources and sinks as well as

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5 their spatial and temporal variation in the atmosphere is still limited (Pozzer et al., 2010). Reliable analytical tools for their accurate measurement in the atmosphere are a prerequisite for a better quantitative understanding of the controlling processes. That is, an accurate and reliable calibration system is an essential requirement for state-of-the-art instruments.

Calibration systems for in-situ instruments rely either on static or dynamic methods (Namiesnik, 1984):

- 10 a. Static methods are based on mixtures of calibration gases stored in closed housings such as high-pressurized gas cylinders with previous wall treatment (Rhoderick and Miller, 1993; Apel et al., 1994, 1998). These calibration cylinders are robust and usually contain a suite of species. However, they are bulky and may suffer, in particular after long storage times, from possible adsorption and chemical reactions of the analyte on the cylinder wall (Barratt, 1981).
- 15 b. In dynamic methods a continuous flow of the relevant analyte is diluted into a carrier gas stream. Dynamic methods most commonly used are mixing of gas streams, diffusion methods, capillary injection, syringe injection and permeation devices (Namiesnik, 1984; Jardine et al., 2010). Diffusion methods and permeation devices are extensively used for the calibration of instruments measuring VOCs in low concentrations (Williams, 1976; Gautrois and Koppmann, 1999; Washenfelder et al., 2003; Jost, 2004; Thompson and Perry, 2009; Veres et al., 2010).

25 Permeation devices usually comprise a short polymer tube sealed at both ends by glass plugs and filled with the analyte of interest. The analyte vapour dissolves into the polymer, diffuses through it, and finally mixes into the sample gas stream. For most analytes, the permeation rate is strongly dependent on temperature. Thus, in order to maintain quantified and constant permeation rates, permeation devices are kept in temperature controlled conditions before and during their use. The time until
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a permeation device reaches an equilibrated state, the so-called stabilization time, typically ranges from hours to days (Williams, 1976).

5 For atmospheric in-situ measurements onboard aircraft, permeation devices have several advantages over high-pressurized gas cylinders. These are the light weight, small volume, and the easiness to meet safety clearance due to the lack of overpressure and the use of only very small amounts of chemicals. However, power loss during transport or before take off due to fuelling of the aircraft can push the permeation system from equilibrium and thus prevent accurate calibration until equilibrium is once again reached.

10 In this paper we describe a new calibration system developed for calibrating our airborne proton transfer reaction mass spectrometers (PTR-MS). Using water as heat buffer, combined with vacuum-panel based insulation and a fast stabilizing permeation membrane, we have conceived a calibration system that has the portability and robustness of regular permeation sources, without the requirement for temperature stabilization. Its actual permeation rate is solely a function of temperature which can be accurately measured. With these characteristics, the presented calibration source is especially suitable for field applications, e.g. onboard aircraft.

2 Calibration devices for VOC measurements

20 A crucial prerequisite for accurate and reliable in-situ measurements of atmospheric VOCs is the generation of known and reproducible gaseous standards at typical ambient mixing ratios. These gaseous standards are essential for calibrating and characterizing either sampling methods, multistep analytical procedures, or online instruments. An overview of applied calibration devices is given by Barratt (1981) and Naganowska-Nowak et al. (2005). Below, the two most widely used techniques for generating calibration standards for VOC in-situ measurements are described, i.e. calibration gas cylinders and permeation devices.

with S the solubility and p the pressure. Combining Eq. (3) with 4 gives the well-known permeation equation (Klopffer and Flaconneche, 2001):

$$J = D \cdot S \cdot \frac{p_2 - p_1}{l} \quad (5)$$

where p_1 and p_2 are the ambient partial pressures on the two sides of the membrane. The product $D \cdot S$ is intrinsic to the membrane material and is defined as the permeability coefficient B :

$$J = B \cdot \frac{p_2 - p_1}{l} \quad (6)$$

This approach, usually known as solution diffusion model (Stannett, 1978; Stern and Trohalaki, 1990), only works for special membrane materials, namely homogeneous non-porous polymers. However, polymers typically used in permeation devices (see below) are porous. Here, adsorption in the polymer and hopping of molecules from pore to pore occur as well, which usually dominate over permeation due to solution-diffusion transport.

The most prominent polymer used in permeation devices is polytetrafluoroethylene (PTFE). PTFE is a porous semicrystalline material (Xiuli et al., 2003; Yi-Yan et al., 1980; Mohamed and Abdel-Hady, 2007), i.e. it is formed of amorphous and crystalline regions. Already 50 yr ago, Michaels and Bixler (1961a,b) showed that sorption and diffusion in semicrystalline polymers take place exclusively in the amorphous regions. The crystalline zones however act as impermeable barriers for diffusion.

To describe the transport in porous materials, the gas transport is parametrized either as viscous (or Poiseuille) flow and/or as Knudsen flow (Fig. 1). Which flow prevails depends on the ratio between the pore diameter d and the mean free path of the gas molecule in the pores λ , called Knudsen number:

$$K_n = \frac{\lambda}{d} \quad (7)$$

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For $K_n \gg 1$ (small pores), where the number of molecule-wall collisions exceeds the one of intermolecular collisions, the permeation is better described by the Knudsen model. For $K_n \ll 1$ (large pores), the permeation follows a viscous flow where intermolecular collisions dominate. For $K_n \sim 1$, the so-called transition flow applies where a combination of both regimes occurs.

According to Kim et al. (2009), λ can be approximated by:

$$\lambda = \frac{\kappa \cdot T}{\sqrt{2} \pi \cdot p \cdot d_m^2} \quad (8)$$

where κ is the Boltzmann constant, p is the pressure, and d_m is the diameter of the gas molecule.

In the following the basic equations describing Knudsen flow and viscous flow are outlined, based on a review by Rutherford and Do (1997) and Choi et al. (2001). Here, the temperature dependence of the permeation rate for both regimes is given and later (Sect. 4) compared with experimental results.

2.3.1 Knudsen flow (small pores)

Knudsen diffusion dominates the transport regime if the pore sizes are small ($K_n \gg 1$). In this case, the analyte flow depends on the concentration difference and hence on the partial vapour pressure difference. In practice, where the permeation device is flushed by an analyte-free carrier gas, the diffusion coefficient depends only on the vapour pressure p_v of the analyte within the permeation device. The diffusion constant for Knudsen flow is parameterized as (Rutherford and Do, 1997):

$$D_K = \frac{d}{3} \sqrt{\frac{8 \cdot R \cdot T}{\pi M}} \quad (9)$$

where M is the molecular weight. The steady state flow is described as (Choi et al., 2001):

$$J_K = D_K \cdot \frac{\epsilon \cdot p_v}{\tau \cdot R \cdot T \cdot l} \quad (10)$$

with ϵ the porosity, p_v the analyte vapour pressure, and τ the tortuosity factor. The latter is in the most simple manner just the ratio between the real pathway a molecule travels through the polymer and the direct path, in our case the membrane thickness / (Epstein, 1989).

Most parameters in Eqs. (9) and (10) are material constants, parameters, or physical constants and thus independent on temperature. Combing them to J_K^0 , the permeation rate described by the Knudsen flow shows the following temperature function:

$$J_K = J_K^0 \cdot \frac{p_v(T)}{\sqrt{T}}, \quad (11)$$

with

$$J_K^0 = \frac{d \cdot \epsilon}{3\tau \cdot l} \sqrt{\frac{8}{\pi \cdot M \cdot R}} \quad (12)$$

2.3.2 Viscous flow (large pores)

If the pore sizes are large compared to the mean free path ($K_n \ll 1$), the number of intermolecular collisions dominate and the flow is governed by viscous flow in the gaseous phase. Such transport, in contrast to Knudsen flow, is driven by the total pressure gradient. The diffusion coefficient is defined as (Rutherford and Do, 1997)

$$D_V = \frac{d^2 \cdot \bar{p}}{32\mu} \quad (13)$$

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where μ is the gas viscosity and \bar{p} the mean pressure within the permeating membrane, i.e. $\bar{p} = (p_v + p_{\text{air}})/2$, with p_{air} the total pressure in the carrier gas. At steady state the flux is (Choi et al., 2001):

$$J_V = \frac{D_V \cdot \epsilon}{\tau \cdot R \cdot T \cdot l} \Delta p \quad (14)$$

where Δp is the pressure difference below/above the membrane or inside/outside the permeation device, $\Delta p = p_v - p_{\text{air}}$.

The gas viscosity μ shows the following temperature dependence

$$\mu = \mu_0(T_0) \cdot \frac{T_0 + C_S}{T + C_S} \cdot \left(\frac{T}{T_0}\right)^{3/2} \quad (15)$$

with $\mu_0(T_0)$ the gas viscosity at the reference temperature T_0 of typically 298.15 K and C_S the Sutherland's constant. As C_S of acetone is with 542 K very high (Hoffmann, 1962), μ roughly scales with $T^{3/2}$. Therefore, the temperature dependence of the viscous flow can be expressed as:

$$J_V = J_V^0 \cdot \frac{(p_v(T) + p_{\text{air}}) \cdot (p_v(T) - p_{\text{air}})}{(T/T_0)^{5/2}} \quad (16)$$

with

$$J_V^0 = \frac{d^2 \cdot \epsilon}{16\mu_0(T_0) \cdot \tau \cdot R \cdot l} \quad (17)$$

2.4 The stabilization time

As outlined in the introduction, one drawback of permeation sources is the long stabilization time, i.e. the time lag between the stabilization of temperature and permeation

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Table 1. Parameters used for calculating the stabilization times for Knudsen flow and viscous flow.

Parameter	Value	Unit
Membrane thickness (l)	0.4	mm
Mean temperature (T)	309	K
Diameter acetone molecule (d_m)	0.63	nm
molecular weight of D6-acetone (M)	64.1	g mol^{-1}
Gas viscosity (μ)	7.9	$\mu\text{Pa s}$
Vapour pressure of acetone (p_v)	467.7	hPa
Air pressure (p_{air})	40	hPa

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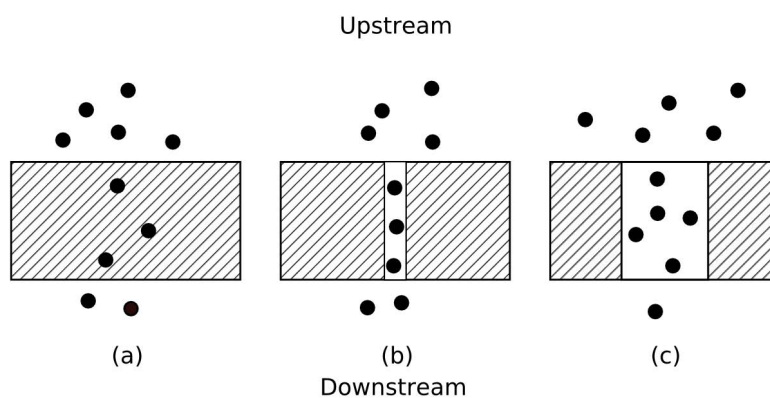


Fig. 1. Permeation mechanisms: **(a)** solution-diffusion based on Fick's law, **(b)** Knudsen flow prevailing at small pores, **(c)** viscous or Poiseuille flow occurring at large pores.

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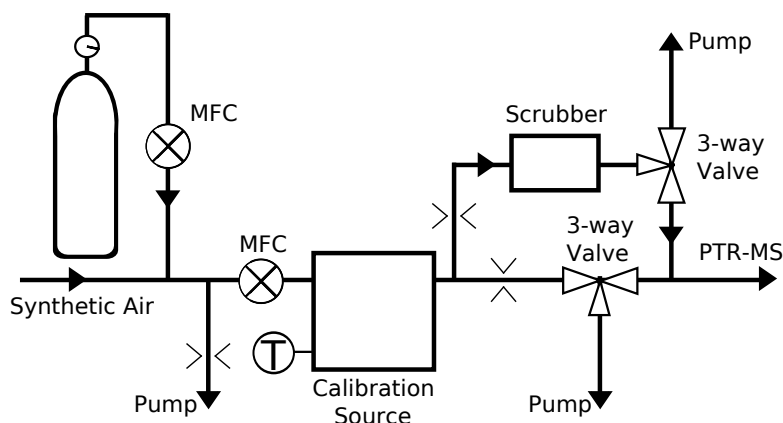


Fig. 2. Experimental setup. Sample air having a well-defined mixing ratio of acetone is generated (left side). For that, air from a cylinder filled with standard gas (Apel-Reimer Environmental, USA) having an acetone mixing ratio of 500 ppbv is mixed with synthetic air. Two mass flow controllers (MFC) lead to a sample gas flow of 35 sccm with an acetone mixing ratio of 16.1 ppbv. This air flow is guided through the calibration gas source filled with isotopically labelled acetone, latter referred as D6-acetone. Thereafter, the air goes either directly into the PTR-MS or before through a VOC scrubber (Pt-catalyst controlled to 350 °C) for measuring the background signal.

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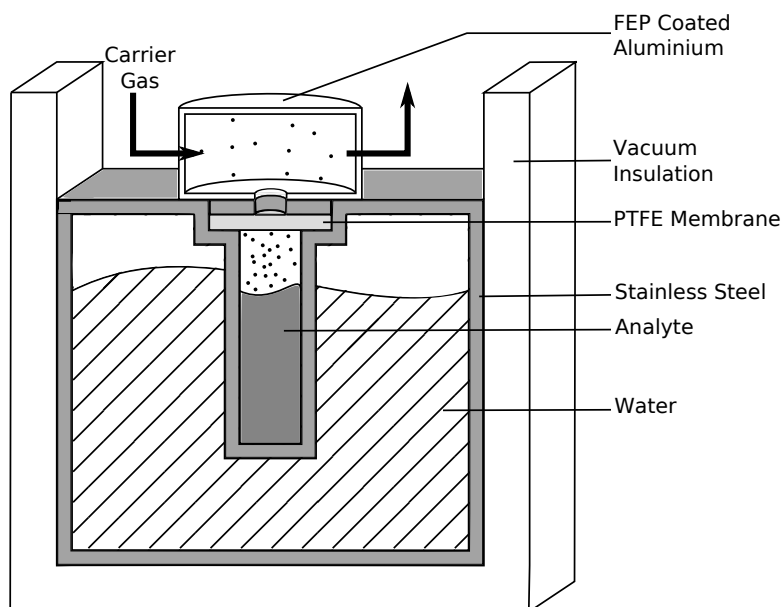


Fig. 3. Schematic view of the calibration system. Five 0.35 ml cylindrical recipients (here, only one is shown) filled with different liquid analytes are surrounded by a water bath. The 0.4 mm thick PTFE membrane works as permeating polymer and provides sealing for the liquid analyte. The "active" area through which permeation occurs is 6 mm². A fluorinated ethylene propylene (FEP) coated aluminium cap sealed with viton O-rings encloses the five permeation membranes. Sample gas enters and leaves the system via perfluoroalkoxy (PFA) fittings fixed into the cap.

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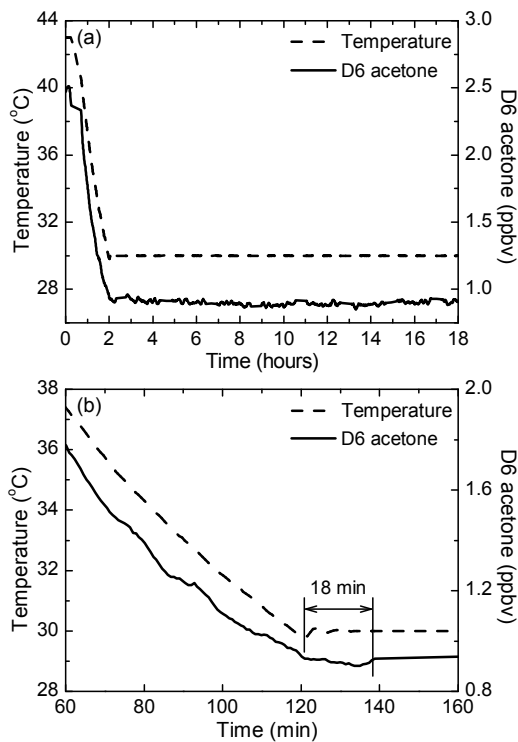


Fig. 4. Temperature of the permeation device (dashed line) and D6-acetone mixing ratio (straight line) during the entire test period of 18 h (graph a) and during 100 min around the stabilization point (graph b).

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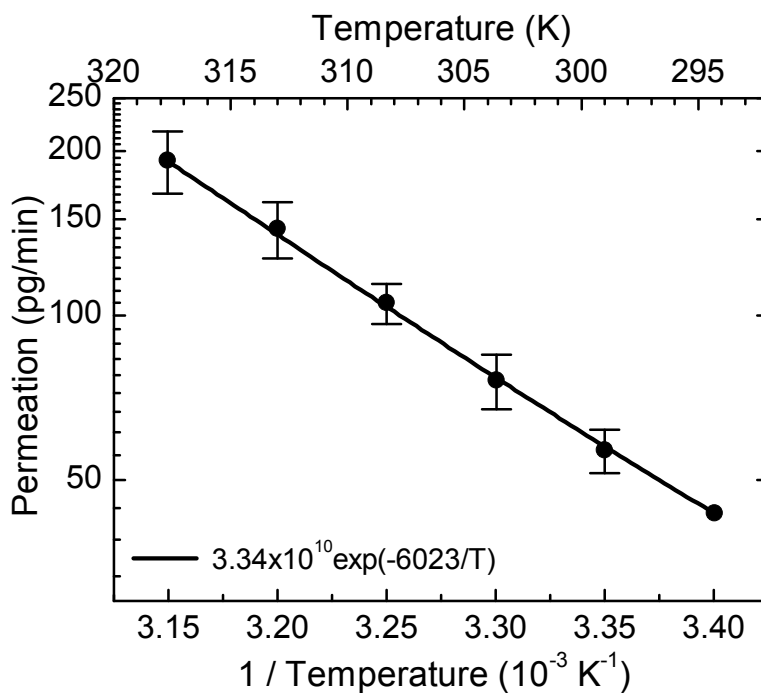


Fig. 5. Permeation rate as function of temperature. Dots: average permeation rate obtained in six temperature cycles and two hours measurement at each temperature step. The standard deviation is indicated by the error bars. At 21°C, only one complete run was achievable. Line: fit to an Arrhenius equation with a correlation coefficient R^2 of 0.999.

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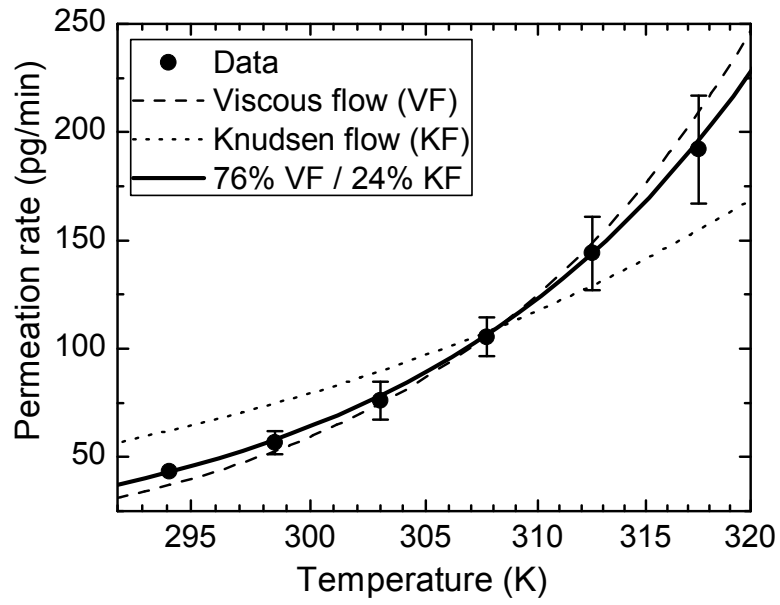


Fig. 6. Permeation rate as function of temperature. Dots: measured data with $1\text{-}\sigma$ variability (error bars). Fit lines for Knudsen flow (dotted, Eq. (11)) and viscous flow (dashed, Eq. (16)). Full line: Combination of both flow regimes, see text.