Specification calculations for Microdrop humidity generator

Harald Sodemann, FARLAB, University of Bergen, Norway

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1 Introduction

Previous studies show a humidity dependency of the isotopic signal reported by the Picarro instruments. Our results and the results by other groups show that this isotope response function, or humidity dependency function, also depends on the water isotope ratio. The results to identify the response surface relative to a reference mixing ratio of 20 000 ppmv require many tedious, and time-consuming calibration runs with different standards. We have performed such runs with the Picarro SDM (A0101) and with the Picarro autosampler and vapourizer liquid injections with variable humidity amounts. Both results provide essentially the same type of response, suggesting that spectroscopy rather than memory is at the cause of this problem. In addition, each analyzer seems to have individual types of this response surface. These and other aspects are being further investigated in collaboration with ETHZ.

Nonetheless, it appears currently necessary that this response function is known when calibrating water vapour measurements at low or variable humidity. To automate the analysis of the isotope-humidity phase space, a different kind of calibration device seems necessary.

A further application for a calibration device is the long-term provision of standard water, over several hours to days. Such a generation of stable calibration gas provides to characterize the Allen variance of an Instrument down to the longer-time range of the spectrum.

This document describes the design of a flexible calibration device serving both of these purposes.

2 Requirements

The calibration device should meet several requirements. These include

1. step through a range of humidities between 100 ppmv and 30 000 ppmv,
2. switch between several standard waters,
3. if possible, provide a mixture of standard waters,
4. provide standard water the range of flow rates by the Picarro from 75 sccm to 350 sccm,
5. provide long-term stable calibration gas at a given setting
6. small, portable system with few parts that can fail

2.1 Existing solutions

These requirements are, in their combination, not met by any existing calibration system. In particular, the SDM provides a more limited range of humidities, with at least 6000 ppmv. The SDM is also limited to two standard waters and allow no easy exchange or mixture of different standards. Injections with the autosampler are feasible with a specific method. Mixture of different standards is also possible before starting the autosampler. However, the mixtures have to be analysed beforehand, or one has to use several lab standards that have been calibrated beforehands. The liquid system can not provide calibration gas at different flow rates.

A further requirements concerns the long-term provision of calibration gas to the analyzer. The Los Gatos WVIS is currently able to produce such a continuous water vapour stream, but shows typically oscillations and variations of the measurement system itself that influence the characterisation of the Allan variance.

3 Design

The calibration device consists of the following main components:

1. a vertically standing evaporation chamber, consisting of a stainless steal chamber with 1/4 inch NPT threads on both ends;
2. two stainless steal tubes of 30 mm length and 10.1 mm diameter, welded horizontally to the upper part of the evaporation chamber;
3. the two tubes are reaching into the interior of the chamber by 3 mm;
4. both tubes hold droplet injection heads (Microdrop GmbH) reaching into the evaporation chamber;
5. each droplet injection head is connected to one 12 ml standard vials mounted besides the evaporation chamber;
6. each droplet injection head is connected to a control device (Microdrop GmbH);
7. at the lower end of the evaporation chamber, a fitting connects a 1/4 inch compression fitting tubing in stainless steel;
8. the 1/4 inch tubing leads in bends through two heated and isolated plates.
9. the plates are heated by thermal heating plates attached to the metal, and regulated electronically;
10. at the entry into the heated tubing, a mass flow controller (MFC) regulates the flow rate electronically;
11. at the upper end of the evaporation chamber, a fitting connects a 1/4 inch compression fitting tubing in stainless steel;
12. a 140 micron filter in stainless steel provides for homogenization of the air as it is leaving the evaporation chamber;

13. a 1/4 inch stainless steel tubing guides to the connection of the analyzer;
14. an external computer controls the MFC, the droplet settings, and the temperature of the calibration device using a LabView software.

Sketches of the instrument design are shown below (Fig. 1).

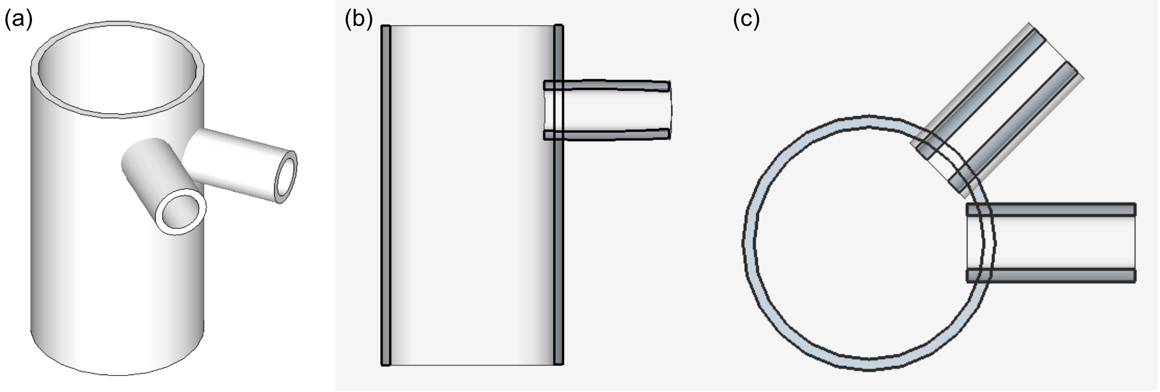

Figure 1: Drawing of the evaporation chamber in (a) 3D perspective, (b) vertical section plane, (d) horizontal section plane.

4 Specifications

Pipe diameters are 45.0 mm at the center of cavity, and 6.0 mm for ordinary 1/4" tubing. This provides cross section areas of 1590.4 mm^2 and 28.3 mm^2, respectively. Volume fluxes in the three operation modes of the Picarro are 30.0, 75.0, 150.0 and 350.0 sccm min^{-1} for low flow, flight mode, and flux mode, and flux mode with high-volume pump. At standard conditions (20°C, 1023.14 hPa), this results in a mass flux of 36.1, 90.3, 180.6 and 421.5 mg min^{-1}, respectively. This corresponds to a gas velocity in the cavity of 0.03, 0.08, 0.16 and 0.37 $\mathrm{cm\,s}^{-1}$. Inside the 1/4" tubing, the gas velocity is 1.77, 4.42, 8.84 and 20.63 $\mathrm{cm\,s}^{-1}$ for the four operation modes. Note that the high-volume pump is currently not in use.

During the time spend in the heating element, which is about 0.75 cm in 1/4" tubing, the air should reach the set temperature of about 60°C. At 25°C, air has a thermal conductivity of 0.026 $\mathrm{W\,m}^{-1}\,\mathrm{K}^{-1}$. The temperature gradient from ambient (20°C) to the metal temperature is ΔT=40°C. The thermal conductivity is a constant in the relation

$$q = -\kappa \cdot \frac{T_2 - T_1}{d} \tag{1}$$

Where q is the heat flux, κ is the thermal conductivity, T_1 and T_2 are two temperatures, and d is a distance. With the heat capacity of dry air at constant pressure $c_p = 1004\,\mathrm{J\,kg}^{-1}\,\mathrm{K}^{-1}$, we can work out whether the air will take up sufficient heat during the travel time of 42.3, 16.9, 8.5, and 3.6 s for the four flow modes. Using Fourier's law, we state that

$$\frac{\partial T}{\partial t} = a \frac{\partial^2 T}{\partial x^2} \tag{2}$$

Here, T is temperature, t is time, x is a position, and a is the thermal diffusivity, given by

$$a = \frac{\lambda}{\rho c_p}. \tag{3}$$

Which needs to be solved with the error function. A simpler solution is available in the so-called regular regime, where the temperature evolution can be approximated by

$$T(t) \approx T(\text{inf}) + Ae^{-\lambda_0 t}. \tag{4}$$

The lowest eigenvalue λ_0 is hereby given by

$$\lambda_0 = \frac{\pi^2 \cdot \kappa}{4\rho \cdot c_p \cdot d^2} \tag{5}$$

In the given situation, we obtain $\lambda_0 = (3.1415^2 \cdot 0.026)/(4 \cdot 1.0 \cdot 1004 \cdot 0.003^2) = 7.0\,\text{s}^{-1}$.

The microdrop generator creates droplets ranging from 35.0 to 90.0 microns. The volume of the droplets is 22.4 to 381.7 pL The corresponding mass is 22.4 to 381.0 ng The terminal fall speed for the two drop diameters is thereby 10.4 and 30.4 cm s^{-1}. At a droplet injection frequency f of 1 to 3000 Hz, the injected water amounts are 0.0 to 4.0 ug min^{-1} for the 35.0 micron drops, and 0.0 to 68.6 ug min^{-1} for the 90.0 micron drops. This results in a range of specific humidities for (i) low flow mode of 0.015 to 44.657 and 0.253 to 759.300 g kg^{-1} for the small and large drops, for (ii) flight mode of 0.007 to 22.329 and 0.127 to 379.650 g kg-1 for the small and large drops, and for (iii) flux mode of 0.003 to 9.569 and 0.054 to 162.707 g kg^{-1} for the small and large drops, respectively. In units of mixing ratio per volume, these numbers correspond to (i) low flow mode of 24 to 69902 and 407 to 835306 ppmv for the small and large drops, for (ii) flight mode of 12 to 35419 and 203 to 495957 ppmv for the small and large drops, and for (iii) flux mode of 5 to 15297 and 87 to 238057 ppmv for the small and large drops, respectively.

With a maximum throughput of $60.0\,\mu\text{L}\,\text{min}^{-1}$, corresponding to a water mass flux of $59.9\,\text{mg}$ min^{-1}, the maximum attainable specific humidity becomes 1657.8 663.1, 331.5 and 142.1 g $\text{kg}^{-1}$for the four modes of operation. In units of ppmv becomes 303944, 759860, 443649 and 210288 g kg^{-1} for the four modes of operation.

Droplets evaporate typically at a time scale of 0.1 and 1.0 s at relative humidity of up to 30%. Fall speeds will progressively reduce, still the largest drops could fall several centimeters before decelerating and evaporating completely. Injection should therefore be done at the top third of the cavity.

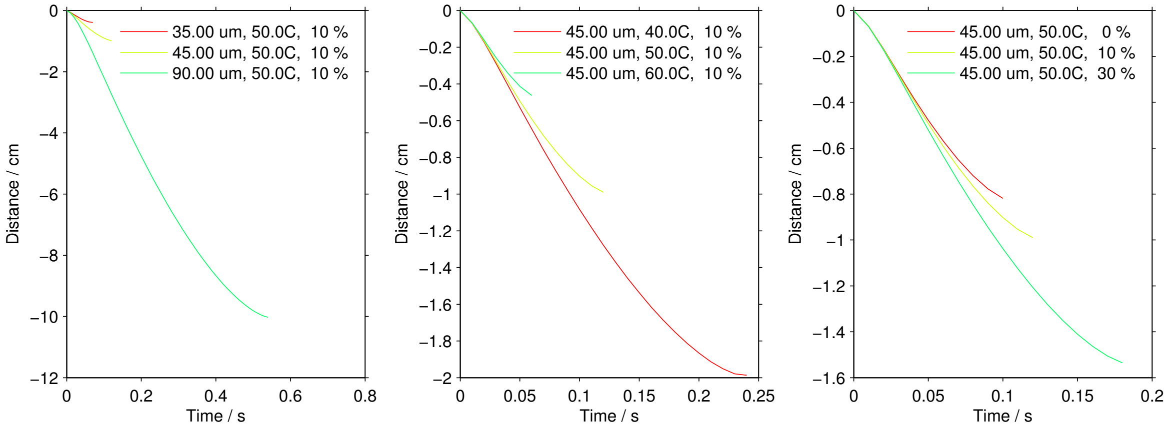

Figure 2: Sensitivity of evaporation of droples in the cavity displayed as trajectory depending on (a) droplet diameter, (b) air temperature, and (c) relative humidity of the cavity air.