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A REVIEW OF CALIBRATION GAS GENERATING METHODS FROM LIQUID SOLUTION OF A COMPOUND

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KEY WORDS

Liquid-in-gas flow, gas permeation, droplets evaporation, calibration gas mixture

ABSTRACT

Over the last decades, the evolution of environmental studies has been tending towards monitoring ever-lower concentrations of pollutants, both in indoor and outdoor air. Therefore, the need for preparing very low concentration gas mixtures to calibrate monitoring devices has been quickly growing. One of the crucial points about preparing such mixtures is generating very low flow rates of a compound in order to achieve very low concentrations.

In addition, some compounds cannot be stored in their gaseous state, such as formaldehyde (HCHO), which is unstable and decomposes easily as a gas. The use of a liquid solution is also more flexible than gases, as it is easier to store and transport. However, creating a gas mixture from a liquid solution of compound requires to evaporate this solution in order to mix it with the carrier gas. Microfluidics help addressing both low flow rates and evaporation issues by bringing ways to manipulate volumes in the order of pico- to microliters inside small and easy to heat devices. At this time, there are several ways to prepare low concentration gaseous mixtures from liquid a solution.

One of them, widely used, is permeation. It consists in slowly evaporating the liquid solution of compound at a known mass flow rate by controlling the temperature [1]. The vapors emitted by the heated solution then pass through a thin porous membrane and diffuse into the carrier gas flow, as shown in Fig.1. Permeation tubes can be found on the market, with mass flow rates commonly ranging from 5 to 50 ng/min (equivalent to 5 to 50 pL/min for pure water). This allows the generation of mixtures of very low concentration without the use of very high carrier gas flow rates, typically 1 to 10 L/min.

Another way is the use of a syringe pump or microfluidic pumps to add a continuous flow of liquid solution to the carrier gas flow. Unlike the previous solution involving permeation membrane, no precise temperature control is required. Instead, a higher heating temperature is needed in order to evaporate the liquid effectively. Very low flow rate syringe pumps provide, for example, an easy way of generating a liquid flow. Pumps can be found on the market with flow rates down to 5 µL/min, however this flow rate is still a hundred thousand times higher than that provided by permeation tubes considering pure water. Such high liquid flow rates require even higher carrier gas flow rates in order to achieve low concentrations of the chosen compound.

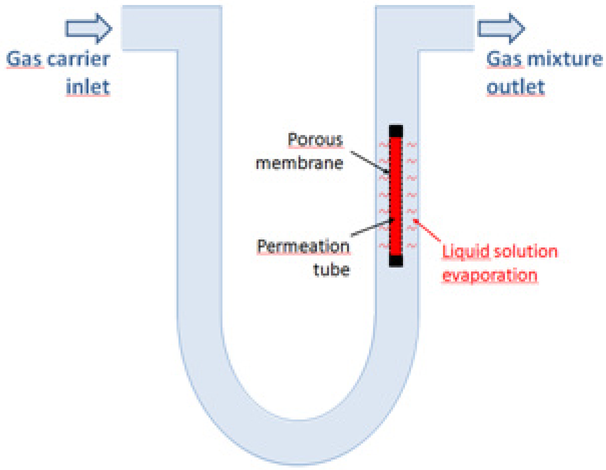

Figure 1:Example of the use of a permeation tube to generate vapors of a liquid solution inside a carrier gas flow. [2]

Another option is to convert the continuous liquid flow into discrete droplets. This allows both very fast evaporation [3] and lower concentration mixtures thanks to the droplets being dispensed periodically, resulting in a lower average liquid flow rate over time, without increasing the carrier gas flow rate. Several methods for dispensing droplets in a gas flow have already been studied, like the one described by Jiang *et al.* [4], shown in Fig.2. In this example, droplets of around 50 to 80 µm diameter are generated and added to a gas flow in a microchannel.

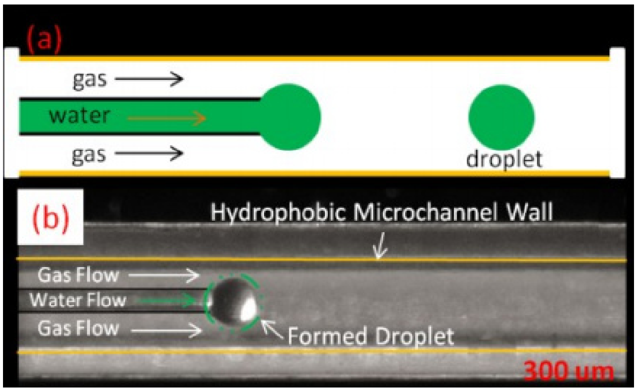

Figure 2: (a) Schematic illustration of the coaxial co-flow droplet generator using gas CP; (b) Microscopic image showing the formation process of a droplet. [4]

The lowest concentrations achieved by all these methods are compared in Tab.1 for a carrier gas flow rate of 1 L/min and an aqueous solution of formaldehyde at 0.01 %w/w concentration (%weight/weight, a mass fraction of the solution). The concentration $C_{CHCHO,gas}$, in ppb, was calculated as follows:

$$C_{\mathrm{HCHO,gas}} = \frac{\dot{\mathrm{m}}_{\mathrm{HCHO}}}{\dot{\mathrm{m}}_{\mathrm{carrier\ gas}}} \quad (1)$$

Equation (1) is then transformed into equation (2) for permeation tube and permanent liquid flow, and into equation (3) for droplets dispensing:

$$C_{\mathrm{HCHO,gas}} = \frac{\mathrm{C}_{\mathrm{HCHO,sol}} \times \rho_{\mathrm{sol}} \times \mathrm{Q}_{\mathrm{sol}}}{\rho_{carrier\ gas} \times Q_{carrier\ gas}} \quad (2)$$

$$C_{\mathrm{HCHO,gas}} = \frac{\mathrm{C}_{\mathrm{HCHO,sol}} \times \rho_{\mathrm{sol}} \times \mathrm{V}_{\mathrm{drop}} \times \mathrm{F}_{\mathrm{drop}}}{\rho_{carrier\ gas} \times Q_{carrier\ gas}} \quad (3)$$

where $C_{HCHO,sol}$ is the concentration in formaldehyde in %w/w of the solution, and ρ_{sol}, Q_{sol}, $\rho_{carrier\ gas}$ and $Q_{carrier\ gas}$ denote respectively the density and the flow rate of the liquid solution and the carrier gas. V_{drop} and F_{drop} are the volume and the dispensing frequency of the droplets.

Table 1: Comparison of the minimum concentration of formaldehyde that can be achieved for each method at 1 L/min of carrier gas flow rate with an aqueous solution of formaldehyde at 0.01% w/w concentration. The liquid flow rate achieved is also presented in this table for each method, considering a solution at ρ = 1090 g/L. For droplets dispensing, 50 µm diameter droplets were considered, dispensed at a frequency of 0.1 Hz.

	Permeation tube	Droplets dispensing	Permanent liquid flow
Q_{sol} (µL/min)	5e^{-6}	3e^{-3}	5
$C_{HCHO,gas}$ (ppb)	0.0005	0.3	500

In this table, we can see that the use of a permeation tube is the best way to achieve very low concentrations of formaldehyde, but these concentrations are way under what monitoring devices can detect, which is usually in the order of 1 ppb. Permanent liquid flow does not facilitate the generation of such concentrations at all, but converting this constant flow into discrete droplets makes it possible to generate ppb levels of the chosen compound.

Furthermore, the variation of concentration in the droplets dispensing method has been studied with changes in carrier gas flow rate and droplets frequency. The results of these calculations are shown in Fig.3.

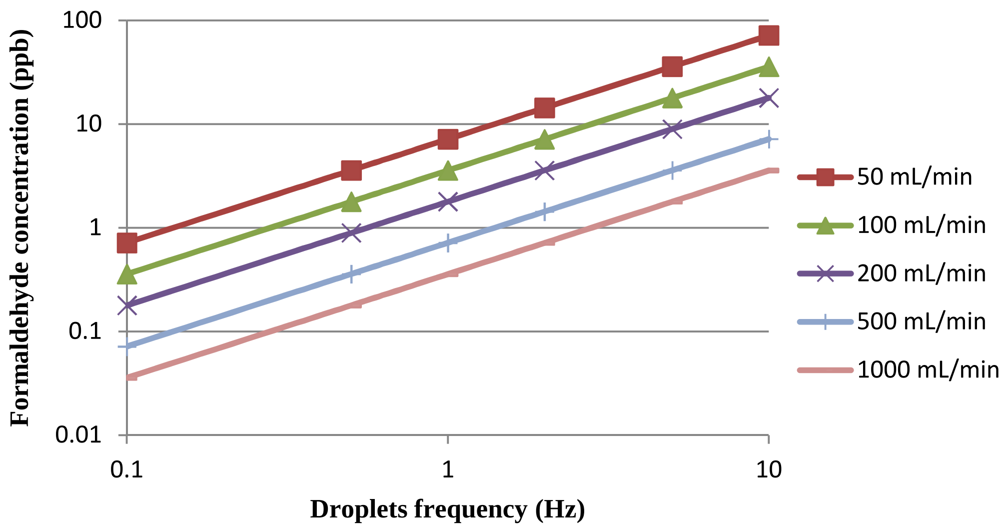

Figure 3: Droplets dispensing frequency versus concentration of formaldehyde at different carrier gas flow rates ranging between 50 and 1000 mL/min.

In this figure, we notice that concentrations in the order of 1 ppb of formaldehyde can be achieved at any carrier gas flow rate, only by changing the droplets generation frequency. It is also shown that 2 decades of concentration can be covered this way. The diameter of the droplets and the concentration of the liquid solution of formaldehyde can also vary in order to change the final concentration of the gas mixture. Therefore, there are 4 parameters that can be individually modified to affect the concentration of the mixture, making this solution much more flexible than permeation tubes.

In this review, the advantages and drawbacks of the different methods for generating a gaseous mixture with a low concentration of a compound previously in a liquid solution are presented. Emphasis is given to the liquid evaporation, as it is the key to achieving homogeneous, totally gaseous mixture. Finally, further investigating the droplets dispensing method opens a brand new wide area of research that might lead to new and effective gaseous mixture generating devices.

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