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MODELLING OF A STANDARD GAS MIXTURES GENERATOR WITH COMPUTATIONAL FLUID DYNAMICS

Guido Sassi [1 2], *Maricarmen Lecuna* [2], *Alessia Demichelis*[1], *MariaPaola Sassi* [1]

[1] Istituto Nazionale di Ricerca Metrologica I.N.Ri.M., Torino, Italy, a.demichelis@inrim.it
[2] Department of Material Science and Chemical Engineering Politecnico di Torino, Torino, Italy,
guido.sassi@polito.it

Abstract – Monitoring VOC for climate change and for indoor and outdoor air quality at trace level concentrations need reference standard materials at high metrological performance. To improve this performance, the description of phenomena involved in mixtures generation by rigorous models is mandatory. A model to describe diffusion cells of a primary generator was developed and validated with experimental data. A good agreement was found between the uncertainties of measurements and calculations.

Keywords: Dynamic generation, reference gas mixture, CFD model, VOC mixtures.

1. INTRODUCTION

The generation of mixtures of volatile organic compounds (VOC) at trace level in air is requested in reference standard preparation [1][2] for measurements of amount of substance fractions or their variations at pmol·mol^{-1} (ppt) and nmol·mol^{-1} (ppb) level. The main applications refer to climate change and air quality monitoring [3][4], industrial Si deposition for electronic and photovoltaic applications [1][5], VOC release from artefacts in domestic and work environments [2][6][7]. Traceable and accurate measurement are requested by organizations to connect the nets of environmental monitoring on the local air quality and global atmospheric watching [3]. Standard mixtures are the reference materials to calibrate sensors and analytical instruments.

Currently, the most common technology to generate standard mixtures are calibrated gas cylinders. Cylinders of reference VOC mixtures at high accuracy are commercially available and behave well at micro level (μmol mol^{-1} as amount of substance fraction) and in the short term (less than 1 year). The challenge is to have high metrological performances at lower concentration to fulfil the needs of applications [3][8][9]. The challenge stresses the need to enhance the description of the main phenomena occurring in the generation device to have a better understanding by detailed simulation of the devices. Dynamic methods continuously provide fresh mixtures with stable VOC amounts of substance fraction and short time VOC interaction at internal tube walls, they are candidate as one of the technologies to fulfil the needs [8][9].

Diffusion generator systems release reproducible accurate and stable amounts of VOC in a flushing carrier gas. Dynamic generation of reference VOC mixtures by diffusion is described by standards [10][11]. VOC release accuracy reproducibility and stability depends on variability and stability of temperature and pressure of the gas-liquid interphase, where phase change occurs, and of the vial pipe, where controlling diffusive transport phenomena occur. Pressure in the vial pipe and on gas-liquid interphase depends on pressure drops of the lines connecting diffusion cell to drain and on atmospheric pressure. Temperature in the vial pipe and on gas-liquid interphase depends on temperature control system, a bath in which cells are partially immerged, heat transfer from controlled zone to the target zones and heat sources and sinks in the generator system.

Standards [10][11] used a simplified modelling approach to fulfil the needs of measurement variability and uncertainty calculation, the approach has been widely discussed and detailed for measurement purposes [12][13]. However, this modelling approach fails when it is applied for design and simulation purposes and cannot help in detailing mass, heat and momentum transfer phenomena which rates determine the smoothing of variability. Non isothermal conditions and local calculation of segregation, mixing and transport enhance the accuracy of description of real systems.

The actual knowledge about diffusion generation is based on the modelling of the ideal diffusion into a pipe through a stationary phase. The boundary conditions are ideally stated at extreme limits of the field, ideal complete mixing is considered in any section of the system. Moreover thermal conditions are maintained stable and reproducible in large systems because the role of thermal wheels, reduced thermal power and high stability of the external control, nevertheless they have a negative effect on dynamics, leading to a long start up time. Computational Fluid Dynamics (CFD) gives an opportunity to do more rigorous calculations to quantify substance concentration and temperature spatial distributions and to account for specific boundary conditions. CFD validated models provides a deep understanding of the phenomena. Simulation over the generation systems allows to evaluate the mass and heat transfer controlling steps toward the design of new devices fitting new geometrical needs or at higher performances.

In this paper, a CFD model is developed to reproduce the experimental results of the diffusion of a liquid VOC to produce a gas mixture. The influence of the changes in geometry and generation conditions is studied. The behaviour and correlations observed can be applied in the definition of the design criteria to generate a stable and reproducible diffusion flow rate.

2. MATERIALS AND METHODS

ANSYS Fluent software was used to develop the model and run simulations. A CFD model was developed to simulate an existing generation setup. A Fick's Law – based Model for Diffusion rate was used to set diffusion rate in a user defined function which interacts with the software in an iterative process. Gas-liquid interphase VOC concentration was calculated and set up as boundary condition. Diffusion rate was experimentally measured to validate the results.

2.1 Generation setup

The generation setup considered for modelling is based on the primary generator device developed by the National Institute of Metrological Research of Italy (INRiM) [14]. The continuous generation of gas mixtures by diffusion is carried out inside cells, where the mass transfer process takes place. Each cell contains a vial containing the liquid VOC to be generated and is constructed to provide an even flow rate of carrier air at a controlled temperature.

The vial containing the liquid VOC reservoir is placed inside the cell (ref. Fig. 1). A thermal bath for temperature control provides a constant temperature (26 or 35 °C) at the external wall of the cell, while sonic nozzles or mass flow controller are installed upstream the generation device, to stabilize the carrier flow rate (dry air at 50 SmL min^{-1} flow rate). Glass is considered as cell and vial material, since it represents an inert surface. A relative pressure up to 3kPa is considered to avoid structural damage of the generation experimental setup. The mixture outlet is placed at the top of the cell, above enough to assure the proper mixing, avoiding uneven concentration of the mixture. Different geometries and generation conditions can affect directly the diffusion flow rate and its uncertainty.

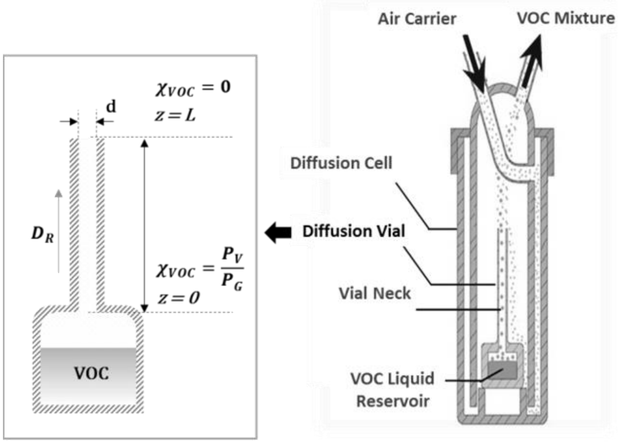

Fig 1. Generation cell and vial scheme.

2.2 Diffusion flow rate estimation

2.2.1 Fick's Law – based Model for Diffusion rate

Diffusion of the VOC from the liquid reservoir through stagnant gas across the neck of the tube is considered. The process of the diffusion can be described as (1) with application of Fick's law to the mass balance along the neck.

$$D_R = \mathcal{D}_{VOC} \frac{\pi d^2}{4L} \cdot \frac{MW_{VOC}}{R} \cdot \frac{P_G}{T} \cdot ln\left(\frac{P_G - p_{z=L}}{P_G - p_{z=0}}\right) \qquad (1)$$

In which $\mathcal{D}_{VOC}$ is the diffusion coefficient of the VOC in air [m^2 s^{-1}], d is the internal diameter of the neck [m], L is the length of the neck [m], MW_{voc}, the molecular weight of the VOC [g mol^{-1}], R is the ideal gas coefficient, P_G is the relative generation pressure, T is generation temperature [K], and p_i are the partial pressures of VOC at the beginning and the end of the neck [Pa].

2.2.2 Gas-liquid interphase VOC amount of substance fraction

Raoult and Dalton equations can be used to calculate the amount of substance fraction of VOC at the gas-liquid interphase. Equilibrium conditions and pure liquid VOC are considered to obtain (2).

$$\chi_i = \frac{p_i}{P_G} = \frac{p_v}{P_G} \qquad (2)$$

Where p_i is the partial pressure of the VOC in the interphase [Pa], p_v is the vapor pressure of the VOC at the interphase temperature [Pa] and P_G is the relative generation pressure [Pa].

2.2.3 Experimental determination of Diffusion rate

The total amount of VOC released from the vial can be determined by periodically weighing the vial. Diffusion rate is calculated as the ratio between the vial mass difference measured over a period of time and the period duration, and can be corrected by the VOC purity and pressure [12]:

$$D_{R,exp} = \omega_{VOC} \cdot \frac{\Delta m}{\Delta t} \cdot \frac{ln\left(\frac{p_{mean}}{p_{mean} - p_v}\right)}{ln\left(\frac{p_{ref}}{p_{ref} - p_v}\right)} \qquad (3)$$

Where ω_{VOC} is the VOC liquid purity [g/g], Δm is the measured mass loss [g], Δt is the period duration between weighings [min], p_{ref} is the reference pressure condition [Pa], p_{mean} is the mean pressure measured in over Δt, p_v is the VOC vapour pressure at the generation temperature.

To obtain the data used in this paper, six vials with two different nominal sizes were considered (ref. Table 1). The chosen VOC for this case study was Acetone.

Table 1. Vials used in experimental data generation

Vial Size	Neck (Nominal) [mm]	Reservoir (Nominal) [mm]	DR @ 26°C (Nominal) [µg.min-1]	# Vials
1	Length 100 Diameter 0.55	Length 30 Diameter 25	1	3
2	Length 50 Diameter 1.2	Length 60 Diameter 25	15	3

Three vials (nominal size 1) were designed at 1 μg min^{-1}, while the other three (nominal size 2) were designed to generate 15 μg min^{-1} of Acetone (nominal diffusion flow rate (@ 26 °C). These vials were weekly weighed for 10 month at 26°C and 35°C. Diffusion rate was calculated as a mean over 5 months of 4 weeks - averaged values. Standard deviation was calculated to be 1% and 0.2% for 1 and 15 μg min^{-1} nominal diffusion rate respectively.

2.3. CFD Simulation Setup

2.3.1 Boundary Conditions

A 2D axis symmetrical geometry of an existing cell was considered for the fluid space inside the cell – vial system. Meshing process was carried out using a CutCell assembly method with a further refinement inside the neck of the vial.

These considerations allowed to obtain a good quality of the mesh, based on the evaluation of the orthogonal quality and aspect ratio as quality parameters. Fig. 2 represents a scheme of the geometry with the boundary conditions used to perform the calculations.

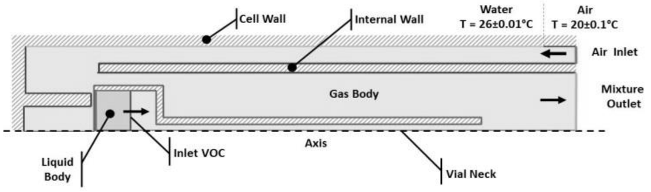

Fig. 2. Geometry and boundary conditions used for CFD simulation.

The definition of the boundary conditions corresponding to carrier inlet and mixture outlet was based on the operative conditions of a typical dynamic generator. [12].

The stagnant liquid could be simulated by using a multiphasic approach or as a different fluid zone. Since there was no particular interest in studying stress effects over the free surface of the VOC, the latter approach was chosen.

The meshing process was done to provide conformity between the meshes, but keeping the possibility of having a wall-wall interface in the gas-liquid interphase.

Additional "interior" boundary conditions were placed at the inlet and outlet of the neck in order to read the local conditions and calculate the diffusion mass flowrate.

2.3.2 Models and Iterative Solver

The species model with inlet diffusion was applied, defining the gas body as a mixture, while the liquid body was defined as pure liquid acetone.

The gas-liquid interface, needed to take into account the mass transfer from the liquid phase to the gas phase, with the respective thermal effect over the liquid reservoir. In this case, the boundary condition was considered as a set of coupled walls, with an amount of substance fraction χ_i defined for the gas side and a heat flow rate set in the liquid side.

The definition of an amount of substance fraction corresponding to the saturation condition at the wall, allowed the software to perform the calculation of the species balance considering Fickian diffusive transport.

The parameters needed to calculate the diffusion flow rate – interphase temperature, amount of substance fractions at the inlet and outlet of the neck- were read using a User Defined Function (UDF). The resulting diffusion rate was used to calculate the heat transferred from the liquid due to the phase change.

The diffusion flowrate was also used to define a mass source term, used to close the continuity balance. The reason is the diffusive transport given by the amount of substance fractions is calculated by the species transport equation and is not included into the continuity equation.

At each iteration, the heat transferred from the liquid and the diffusion flowrate were assigned. The first, at the liquid side of the wall-wall boundary condition, while the source term was included in the cell layer adjacent to the gas side of the wall.

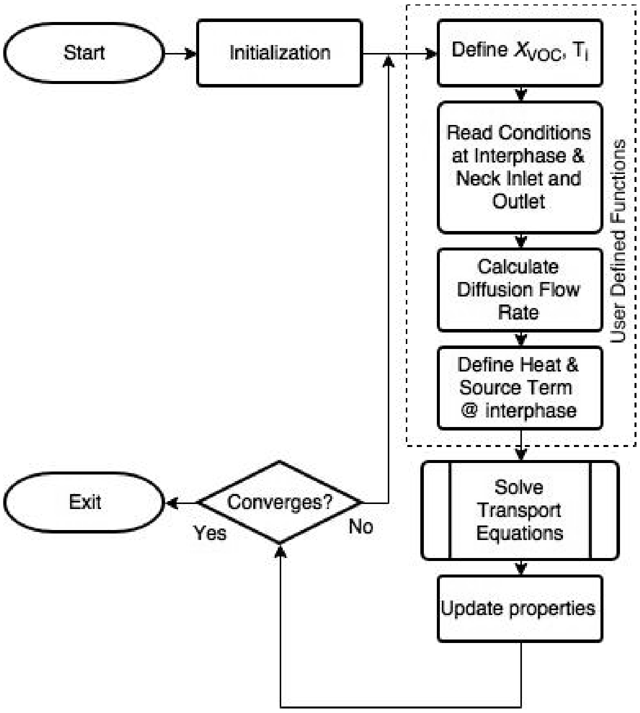

Fig. 3. Simplified Flowchart for ANSYS Fluent Calculation

With this conditions, the solver performed further heat and mass transfer calculations over the whole domain. This process continued until convergence of all the balances. Fig. 3 represents a simplified flowchart on how the UDFs are integrated into the Fluent solver.

The use of this method gives as result a CFD model that considers the combined effect of the premises considered by the theoretical model showed above and the fluid dynamics calculations made by the software.

3. RESULTS AND DISCUSSION

3.1. Model Performance Evaluation

3.1.1. Uncertainty evaluation

An uncertainty budget was made to evaluate the sources of uncertainty of the CFD model “measurand”: the diffusion flow rate. The uncertainty analysis was done considering the influence of the neck length and diameter, the reservoir diameter, the liquid level inside the vial, the diffusion coefficient, the thermal coefficient of liquid VOC, the heat of vaporization of the VOC and the temperature and pressure of generation.

Using the Guide to the expression of Uncertainty in Measurement (GUM) procedure [15], the propagation of the uncertainties of each parameter into the measurand was calculated. The sensitivity coefficients were calculated by changing the different parameters of the model and evaluating the results.

The budget allowed to identify the main sources of uncertainty of the model and to obtain the estimated uncertainty of the theoretical diffusion rate based on its influence variables.

The significance index (SI) of a variable can be defined as the ratio between the contribution to uncertainty of that variable and the maximum contribution [12]. This indicator allows to identify the variables representing the main sources of uncertainty. A generation using the two vial sizes was considered at 26°C, and the significance index of each variable was calculated. From these analyses, the main sources of uncertainty for both configurations were the neck diameter (SI% = 100% and 83% for vial size 1 and 2 respectively) and the diffusion coefficient (SI% = 16.9% and 3.5% for vial size 1 and 2 respectively). The total estimated uncertainty for vial size 1 and 2 were 13.5% and 2.2% respectively.

3.1.2. Validation of the Model

The characterization of two existing vials was made and the results were used to evaluate the performance of the theoretical model. The effects of the temperature and geometry over the diffusion flow rate were calculated using the CFD model and compared with the experimental results.

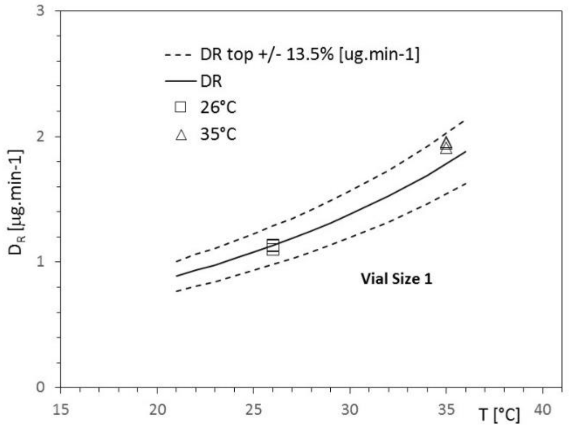

Fig. 3. Model validation for Vial Size 1.

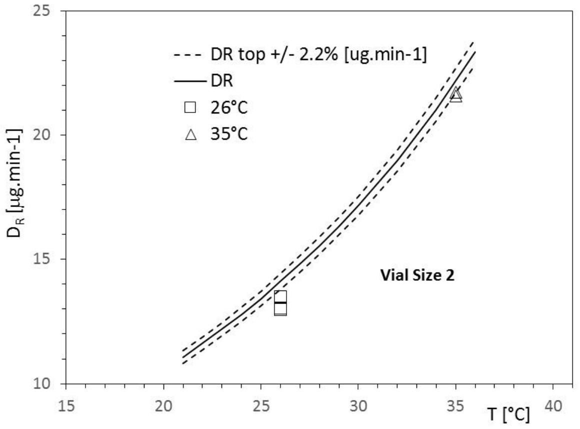

Fig. 4. Model validation for Vial Size 2.

Four experimental set ups were considered for validation (Vials sizes 1 and 2 (ref. Table 1) with acetone at 26°C and 35°C). For the comparison, a sensitivity analysis of the CFD model over the temperature was made for each vial size. The comparison between experimental and CFD model results for each vial configuration, are shown on Fig. 3 and Fig. 4.

From the validation charts, it can be observed that the simplified CFD model developed is able to predict the diffusion rate considering the thermal effects for different geometries.

The weight of the neck diameter into the final uncertainty was due to the uncertainty of the measurement. Using an instrument providing a least count in the order of 1 micrometer would minimize the uncertainty to 5.2% and 0.5%, for vial size 1 and 2 respectively.

4. CONCLUSION

A combined model to describe the behaviour of generation diffusion cells with inner vial was developed. ANSYS Fluent software was used to simulate the thermal effects and momentum transport inside a typical generation cell. Additionally, a simplified theoretical model was introduced using a UDF to define the heat and diffusive mass transfer in the gas – liquid interface.

The uncertainty of the CFD model was estimated and the main sources of uncertainty identified, which resulted to be the diffusion coefficient and the neck length and diameter. These results could be used to estimate the required uncertainty of each parameter to minimize their significance index to a negligible impact (SI% below 1%). Finally, the validation of the model was made, by comparing a sensitivity analysis of the CFD made over the temperature for acetone, with six experimental points for each of the two vial sizes considered. The model provided a good fit for the experimental data for both cases, and can be used to perform further sensitivity analyses to develop a set of criteria to design cells that can effectively produce a reproducible diffusion flow rate.

5. ACKNOWLEDGMENTS

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