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DIFFUSION VIALS FOR LOW AND ACCURATE RELEASE OF KEY-VOC IN ATMOSPHERIC CHEMISTRY AND CLEAN ROOM INDUSTRIES

Alessia Demichelis[1], *Guido Sassi*[1 2], *Maria Paola Sassi*[1]

[1] Istituto Nazionale di Ricerca Metrologica I.N.Ri.M., Torino, Italy, a.demichelis@inrim.it
[2] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Torino, Italy, guido.sassi@polito.it

Abstract: Accurate VOC mixtures at ppb level are needed both for the atmospheric monitoring both for the clean room industries. Research is developing a compact diffusion generator of trace mixtures to be installed on-site. To assure the required accuracy, vials with a low and calibrated diffusion rate DR are necessary. In this paper glass vials were realized, the uncertainty budget of DR was evaluated and experimentally validated. A DR accuracy better than 3% at 200 ng/min release rate was obtained.

Keywords: Key-VOC, AMCs, reference gas mixtures, diffusion rate, uncertainty.

1. INTRODUCTION

Accurate and stable gas mixtures of oxygenated volatile organic compounds at ppb level, such as acetone, ethanol and methanol, are needed both for the atmospheric chemistry monitoring community [1] both for the clean room industries [2].

Methanol (CH3OH) is formed in the atmosphere as a common product in the degradation mechanisms of many primary hydrocarbons. The rationale for its long term observations is that its generation and its future abundance is extremely difficult to predict, since it is an end product of oxidation processes. Its abundance changes in the longer term must be monitored since it is a tracer of anthropogenic emissions, oxidation processes and biosphere releases [3].

Ethanol (C2H5OH) is a larger oxygenated VOC with a diverse range of sources including direct anthropogenic emissions, biosphere emissions and atmospheric oxidation of higher hydrocarbons. Longer-term measurements are needed to determine its global trend as it is introduced as a carbon cycle-neutral component of fuels. The influence of ethanol in the background atmosphere, under future energy supply scenarios, is not clear and needs to be assessed [3].

Acetone (C3H6O) is another oxidation product of higher hydrocarbons with reasonable atmospheric stability. Its future behaviour is strongly dependent on the atmospheric transport pathways and on the future releases of hydrocarbon species in addition to non-linear oxidation chemistry. It is therefore essential that its longer-term behaviour is determined since it is at the centre of both emissions and oxidation processes [3].

The most effective means of prepare reference standards, accurate and stable, for oxygenated VOC measurements are dynamic generation methods, such as diffusion generation [4]. This method consists in the mixing of the component mass flow rates (VOC flow from diffusion vials and dilution air flows) [4]. Research is ongoing to develop a compact generator of stable trace VOC mixtures for the on-site calibration of gas analysers at climate monitoring stations [1].

Different classes of Airborne Molecular Contaminants AMCs in the wafer production area of clean room industries include Volatile Organic Compounds VOCs at sub-ppb level. For some processes, such as advanced lithography, very small quantities of VOC, in particular "high molecular weight/high boiling point" (e.g., C6-C30) hydrocarbons are detrimental because of the increased adherence to the exposed surfaces, and the potential for photochemical degradation that leaves non-volatile residues on lenses, masks, mirrors, etc. However, any VOC, even ones with retention times less than C6, like acetone, are considered detrimental if they can result in refractory deposits. In order to detect such species with ultimate sensitivity, it is necessary to directly detect the relevant species and calibrate the analyser with the appropriate standard. These standards are currently virtually non-existent for AMCs. The main reason for this is that AMCs cannot be stored in cylinders due to their high reactivity and/or low vapour pressure. Dynamic gas generation methods, such as diffusion, with suitable stability and accuracy can allow the calibration of AMC analysers. A compact AMC diffusion generator to be installed on-site can realize the required standard mixtures for analyser's calibration [2][5].

To assure the required accuracy for the dynamic generation of VOC gas mixtures in both fields, vials with a calibrated diffusion rate are necessary. This is because the diffusion rate is one of the main uncertainties of the reference mixtures. Calibrated vials will avoid the problem of accurate weighing loss measurement of the VOC inside a compact generator. In the case of a compact generator, the consumption of dilution air flow is limited. It follows that a lower diffusion rate, comparable with the release rate by permeation tubes, is required for the realization of VOC mixtures at trace level (sub-ppb). At this low release rate (below 1 ug/min) a comprehensive metrological study must be conducted in order to limit uncertainty of DR.

In this paper performances of diffusion vials, designed for low release rate, are presented. The vials were designed and realized, the uncertainty budget of DR was evaluated and validated by experimental gravimetric measurements.

2. MATERIALS AND METHODS

3.1 Diffusion vials

The diffusion vials were realized in borosilicate glass, as shown in Fig.1, welding an open tube to a tank of 2 cm o.d. in which the liquid VOC was inserted. The diffusion tubes with i.d. in the range 0.6 – 2.2 mm and length in the range 5 – 10 cm were employed to provide nominal DR in the range 0.2 – 40 ug/min, at 26°C.

Fig. 1. Picture of diffusion vials realized.

The vial tanks were ¾ filled with oxygenated VOCs, like acetone, methanol, ethanol and acetonitrile and inserted in ad-hoc diffusion cells placed in a thermostatic bath (model HAAKE DL30/W46B). The vials were thermostated at 26 ± 0.015 °C and continuously flushed with a 50 Sml/min purified air flow. This is done in order to maintain the boundary conditions of the based diffusion Fick's model [6], and in turn maintain a stable DR.

3.2 Diffusion rate measurements

Diffusion rates were measured by weekly weightings of diffusion vials using an analytical balance (Mettler Type H15) with resolution 0.1 mg and with an analytical balance (Sartorius CPA225D) with resolution of 0.01 mg. The vial pressure was measured on the upstream of the diffusion cell by a barometer with a 30 Pa calibration uncertainty (model MKS Baratron Type 310BHS-1000 Pressure Head with a type 170M-6C electronics).

The DR at the actual pressure condition of 101325 Pa, was calculated using the following equation, obtained from [7]:

$$DR_{actual} = \omega_{VOC} \cdot \frac{\Delta m}{\Delta t} \cdot \frac{ln\left(\frac{p_{actual}}{p_{actual} - p_v}\right)}{ln\left(\frac{p_{mean}}{p_{mean} - p_v}\right)} \qquad (1)$$

In which ω_{VOC} is the VOC liquid purity [g/g], Δm is the measured weigh loss [g], Δt is the reference time interval [min], p_{actual} is the actual pressure condition of 101325 Pa, p_{mean} is the mean vial pressure measured over Δt, p_v is the VOC vapour pressure at 26°C.

Data of DR from 35 diffusion vials were obtained by weekly weightings performed in a 6 years period. The DR over a monthly period were calculated by the sum of the weekly weigh loss obtained. The variability of experimental DR was calculated as relative standard deviation of obtained data. The experimental variability was compared with the calculated uncertainty.

3. RESULTS AND DISCUSSION

3.1 DR uncertainty budget

In Table 1 the DR uncertainty budget for a DR of nominally 5 ug/min, weekly determined with the more accurate balance, is reported. dp_{actual} and dT_{actual} represent the stability of pressure and temperature of the diffusion vial in the observing Δt. Quantity X, unit of measure [X], mean value x, standard uncertainty u(x), relative standard uncertainty u(x)/x and significance index IS are reported. The explanation of influence quantities and quantification of uncertainty sources was done in [7].

The main uncertainty source, when low DR are realized, is given by the weight loss measurement. Opportunities to reduce DR uncertainty can be found improving weighing accuracy u(Δm) and increasing weigh loss Δm.

In Fig. 2 the DR uncertainty is calculated in function of DR for different weighing accuracy and durations, the results are reported as solid curves. The calculations were done for acetone. For low DR, these calculations can be compared with experimental data of other VOCs. This is because the vapour pressure gives a negligible contribution, as shown in Table 1.

Table 1. Diffusion Rate uncertainty budget.

X	**[X]**	**x**	**u(x)**	**u(x)/x**	**IS**
Δm	g	0.2016	0.0008	0.40 %	100 %
Δt	min	40320	7	0.02 %	0 %
p_{mean}	Pa	98000	58	0.06 %	2 %
p_{actual}	Pa	101325	58	0.06 %	3 %
p_V	Pa	12382	371	3.00 %	0 %
ω_{VOC}	g·g^{-1}	0.999	0.0006	0.06 %	2 %
dp_{actual}	Pa	0	50		2 %
dT_{actual}	K	0	0.015		11 %
DR_{actual}	**µg·min^{-1}**	**4.820**	**0.020**	**0.44%**	

To validate the opportunities for DR uncertainty improvement at low release rate, a more accurate analytical balance and a DR calculation based on a monthly weigh loss could be considered.

3.1 Validation of DR uncertainty at low release rate

In Fig.2 the experimental variability of DR measurements are reported as points.

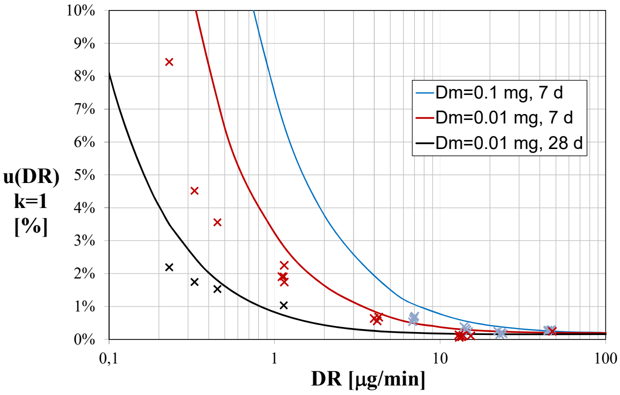

Fig. 2. Experimental DR variability in comparison with calculated DR uncertainty for different weighing accuracy (0.1 or 0.01 mg) and periodicity (7 or 28 days).

The following information can be outlined:

- The evaluated uncertainty budget (Table 1) [7] is validated by the gravimetric experimental measurements in the tested range of DR 0.2 – 50 ug/min. The experimental variability is congruent and lower than the calculated uncertainties.
- The use of a more accurate balance allows to obtain more reproducible and accurate DR measurements.
- The DR calculation for a monthly periodicity allows a 4-fold enhancement of DR accuracy for the lowest DR (0.2 ug/min).

4. CONCLUSION

In this paper, performances of diffusion vials for preparation of reference gas mixtures at trace level are discussed. The developed method allowed to realize DR in the requested lower range, typical of permeation tubes, with an uncertainty lower than 3% at 200 ng/min. To reach this result a 0.01 mg analytical balance was used with weekly weightings of the diffusion vials and with a diffusion rate calculated over a monthly period.

Vials calibrated at low release rate have the potential to be employed in compact diffusion generators. They can be used for the preparation of reference gas mixtures for on-site traceable calibration of gas analyzers. The availability of reference mixtures of key oxygenated VOC will improve measurement accuracy for the atmospheric monitoring community and the clean room industries.

5. ACKNOWLEDGMENTS

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