

A DYNAMIC TRACE VOC GENERATOR USEFUL FOR GLOBAL CLIMATE CHANGE STUDY

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Abstract — With the goal of the realization of a primary standard of amount-of-substance fraction of VOC (Volatile Organic Compounds) at trace level, a dynamic generator is constructed, based on the diffusion phenomena, according to ISO 6145-8. Generator will be followed by a dilution system. In the present paper, generator performances are discussed.

The analysis of ISO 6145-8 shows that temperature control gives the main contribution to uncertainty. The use of a more precise temperature and evaporated VOC mass results to be the main contribution. Weekly measurements of diffusion rate demonstrate the correct uncertainty calculation and the enhances due to the more precise temperature control. Uncertainty of diffusion rate was calculated as composed uncertainty of measured variables to be 0,4% for 20 µg/min by weekly measurements instead 0.8% calculated for the ISO 6145-8 conditions. Type A calculation of uncertainty on experimental data, corrected by pressure, confirmed theoretical uncertainty calculation.

Keywords: VOC, diffusion rate, climate change, dynamic reference mixtures

I. INTRODUCTION

The World Meteorological Organization (WMO) programme is designed to monitor and document changes in atmospheric composition over long time periods (decades) to study the global climate change models [1].

These models are strongly influenced by the incomplete knowledge of the global distribution of the chemical compounds responsible of climate change. The task of chemical compounds monitoring is assigned to the network Global Atmosphere Watch (GAW), globally distributed (Fig. 1), measuring a wide range of compounds, included the ozone-precursors VOC – Volatile Organic Compounds.

In fact, these compounds, even though present in the atmosphere in small amount (from 0.01 ppb_{mol} to 10 ppb_{mol}), are a cause of global climatic change for their ability to catalyze chain reactions stimulated from sunshine and to act as aerosol-precursors.

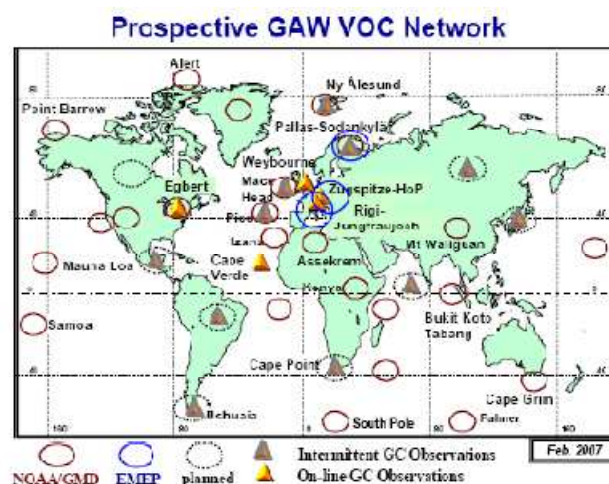


Fig. 1. The GAW VOC network

Nowadays the traceability of the measurements within global stations is assured only by the use of standard mixtures of pure hydrocarbons certified in high pressure gas cylinders by different NMIs. These cylinders are affected by long-term instability for VOC, like monoterpenes, oxygenated VOC, acetonitrile and DMS, at these trace levels. To overcome this problem, the GAW asked to NMIs to develop calibration procedures (realization of primary gas standards) for these VOC at trace levels advantaging dynamic generation techniques because of the better long-term stability properties.

The ISO 6145-8 standard [2] defines the preparation method of dynamic volumetric calibration gas mixtures based on diffusion. This standard specifies a method for the preparation of calibration gas mixtures containing component mole fractions ranging from 10^{-9} to 10^{-3} . The standard states the main sources of uncertainty to be taken into account when a precise evaluation of the uncertainty budget of the prepared mixtures has to be done.

The conclusions of ISO 6145-8 are that this method allows to reach a relative expanded uncertainty of the generated amount-of-substance fraction not greater than $\pm 2\%$. For the component mass flow (or "Diffusion Rate") is estimated an uncertainty of $\pm 0,5\%$ ($k=1$).

In this study a dynamic generation system for VOC at trace level is constructed and the Diffusion Rate uncertainty is evaluated by considering the uncertainty sources defined in ISO 6145-8. The analysis of the relative weights of uncertainty components of the budget shows that the temperature variability drastically influences the Diffusion Rate uncertainty.

In INRIM has been chosen a generation system with a control of the temperature better than one order of magnitude in respect to which considered in the standard. In this way the uncertainty contribution due to T variability is significantly decreased, the differential mass measurement became the major contribution (mainly¹ due to buoyancy effects) and the Diffusion Rate uncertainty halved.

The experimentally estimated uncertainty confirm the theoretical evaluation.

II. UNCERTAINTY BUDGET ANALYSIS¹

Table 1 shows the accuracy budget for Diffusion Rate DR at the conditions proposed by ISO 6145-8, this was calculated for the diffusion VOC generator by:

$$DR = \frac{\Delta m}{\Delta t} \frac{p_{mean}}{p_{actual}} + [gX_3 \delta p_{mean} + g(X_1 + X_2) \delta T_{mean}] \quad (1)$$

Table 1. Diffusion Rate Budget at ISO conditions

X	[X]	x	u	u/x	[c·u] ²	RI	AI
Δm	mg	207,76	0,61	0,29%	2·10 ⁻¹⁶	15%	12%
Δt	min	40320	1,4	0,004%	3·10 ⁻²⁰	0%	0%
p _{mean}	Pa	98308	100	0,10%	2·10 ⁻¹⁷	2%	2%
p _{actual}	Pa	101325	113	0,11%	3·10 ⁻¹⁷	2%	2%
δp _{mean}	Pa	0	100		3·10 ⁻¹⁷	2%	2%
δT _{mean}	K	0	0,087		1·10 ⁻¹⁵	100%	83%
DR	μg/min	5,000	0,041	0,83%	2·10 ⁻¹⁵		

Table 2. Diffusion Rate Budget at 0,01 K temperature control

X	[X]	x	u	u/x	[c·u] ²	RI	AI
Δm	mg	207,76	0,61	0,29%	2·10 ⁻¹⁶	100%	66%
Δt	min	40320	1,4	0,004%	3·10 ⁻²⁰	0%	0%
p _{mean}	Pa	98308	100	0,10%	2·10 ⁻¹⁷	12%	8%
p _{actual}	Pa	101325	113	0,11%	3·10 ⁻¹⁷	15%	10%
δp _{mean}	Pa	0	100		3·10 ⁻¹⁷	15%	10%
δT _{mean}	K	0	0,01		1·10 ⁻¹⁷	9%	6%
DR	μg/min	5,000	0,018	0,36%	3·10 ⁻¹⁶		

¹ In the tables, X represents the variable, [X] the unit of measure, x the value, u the standard uncertainty, u/x the relative uncertainty, in [c·u]² the c is the sensitivity coefficient, RI the relative index, AI the absolute index.

All DR relative uncertainties are for k = 1.

The budget of uncertainty was calculated on the basis of GUM [4] suggestions, it's shown that temperature gives the main contribution to uncertainty (Relative index RI=100%).

ISO 6145-8 indicates 0,50% as relative uncertainty of diffusion rate on the basis of Type A uncertainty calculation on experimental diffusion rate evidences.

Temperature control systems at nominal 0,01 K precision are commercially available. Table 2 shows the budget of uncertainty with closer temperature control.

The main contribution to uncertainty come from VOC mass difference (RI=100%, RA 66%). Pressure variability and correction have not a negligible contribution to uncertainty (RI>10%). Temperature variability have a almost negligible contribution (RI=9%). Total theoretical uncertainty is around halved and lower than the type A uncertainty declared by the ISO 6145-8.

III. EXPERIMENTAL

VOC generator by diffusion tubes was design and realized following the principles reported in ISO 6145-8 and considering diffusion model [3].

Figure 2 show a schematic drawing of the generation and dilution system.

The dynamic trace CH₃CN generator

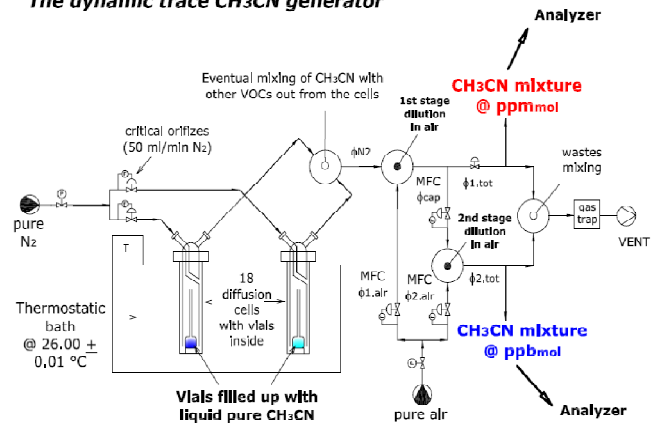


Fig. 2. The dynamic trace generator scheme

Temperature was controlled at 26°C at less than 0,01 K variability. Performances of temperature control were experimentally verified. Room temperature was controlled at 20°C at 0,2 K variability.

Pressure was monitored by barometer at 3 Pa calibration each 30 min. Observed pressure variability was calculated as the maximal standard deviation of the mean on single weeks in the last 2 years. Pressure variability was observed to be lower than 50 Pa at all period considered (from minute to year).

3 vials were used for 20 μg/min nominal Diffusion rate.

VOC mass change was measured by an analytical balance at 0,5 mg calibration, weighting time for vials was verified to be lower than 5 min.

Around weekly weighting were performed for the 3 vials over 3 months. Diffusion Rate was calculated as:

$$DR = w_{voc} \left\{ \frac{\Delta m}{\Delta t} \frac{p_{mean}}{p_{actual}} + [gX_3 \delta p_{mean} + g(X_1 + X_2) \delta T_{mean}] \right\} \quad (2)$$

Where w_{voc} is the mass fraction of VOC in liquid VOC, Δm the difference between two vial weights, Δt the time between two weighting, p_{mean} is the mean of pressure measurements on the period between the two weightings. p_{actual} is the single pressure measurement (stated at 101325 Pa as reference for the Diffusion rate measurement), δp_{mean} and δT_{mean} are variability of pressure and temperature on the period between the two weightings and $g X_1, X_2, X_3$ are the sensitivity coefficients of diffusion rate model in stagnant film [2]. 20 $\mu\text{g}/\text{min}$ as nominal diffusion rate was chosen 4 times of that considered in ISO 6145-8 in order to have mass difference similar to that considered in ISO 6145-8 on 4 week period.

Acetonitrile CH_3CN was chosen as model VOC (vapour pressure similar to Benzene considered in ISO 6145-8, but safer for handling).

IV. RESULTS

Vials were designed for a nominal diffusion rate of 20 $\mu\text{g}/\text{min}$ in order to reach the same mass difference for 4 weeks at 5 $\mu\text{g}/\text{min}$ as considered in the ISO 6145-8.

Table 3 shows the budget of uncertainty of equation (2) for weekly diffusion rate of 20 $\mu\text{g}/\text{min}$ at ISO 6145-8 conditions (0,1 K for temperature variability). Temperature variability is the main (relative index $\text{RI}=100\%$) and the only (absolute index $\text{AI}=94\%$) contribution to diffusion rate uncertainty. All the other variables have a irrelevant (relative index $\text{RI}<10\%$) or negligible (relative index $\text{RI}<1\%$) contribution to diffusion rate uncertainty.

Table 4 shows the budget of uncertainty of equation (2) for weekly diffusion rate of 20 $\mu\text{g}/\text{min}$ at the experimental INRIM conditions (0,01 K for temperature variability). Mass difference is the main (relative index $\text{RI}=100\%$) and almost the only (absolute index $\text{AI}=86\%$) contribution to diffusion rate uncertainty. All the other variables have a irrelevant (relative index $\text{RI}<10\%$) or negligible (relative index $\text{RI}<1\%$) contribution to diffusion rate uncertainty. Theoretical uncertainty calculated by the budget is reduced from 0,77% to 0,39% operating at the experimental conditions (the main change is temperature control).

Diffusion rate was calculated by equation (2) for each weekly measurement and for each vial. Mean value x , Type A uncertainty (standard deviation) of Diffusion Rate are reported in Table 5 for each vial.

Uncertainty calculated from experimental measures is lower than theoretical uncertainty calculated by the budget. Always lower than the 0,5% considered by the ISO 6145-8 from Type A uncertainty calculations.

Table 6 reports the composed uncertainty for a nominal diffusion rate of 5 $\mu\text{g}/\text{min}$ measured on 4 weeks period.

Referring to Table 4 the Diffusion rate uncertainty value is similar, absolute indexes (AI) and relative indexes (RI) of single variable contribution are similar.

From the comparison of Table 6 with Table 2 it is possible to state that the use of a less accurate balance (INRIM balance = 0,5 mg; ISO = 0,05 mg) is compensated by the reduced pressure variability observed at INRIM (INRIM = 50 Pa; ISO = 100 Pa). They lead to similar evaluated DR uncertainty (Table 6: 0,38%; Table 2: 0,36%).

Table 3. Diffusion Rate Budget at ISO conditions
Nominal DR 20 $\mu\text{g}/\text{min}$ over 1 week

X	[X]	x	u	u/x	$[c \cdot u]^2$	RI	AI
Δm	mg	206,60	0,17	0,08%	$3 \cdot 10^{-16}$	1%	1%
Δt	min	10080	1,4	0,01%	$1 \cdot 10^{-17}$	0%	0%
p_{mean}	Pa	98981	100	0,1%	$6 \cdot 10^{-16}$	2%	2%
p_{actual}	Pa	101325	0	0%	0	0%	0%
δp_{mean}	Pa	0	100		$7 \cdot 10^{-16}$	2%	2%
δT_{mean}	K	0	0,087		$1 \cdot 10^{-14}$	100%	94%
w_{voc}	g/g	0,999	0,0006	0,06%	$2 \cdot 10^{-16}$	1%	1%
DR	$\mu\text{g}/\text{min}$	20,000	0,153	0,77%	$3 \cdot 10^{-14}$		

Table 4. Diffusion Rate Budget at INRIM conditions
Nominal DR 20 $\mu\text{g}/\text{min}$ over 1 week

X	[X]	x	u	u/x	$[c \cdot u]^2$	RI	AI
Δm	mg	206,60	0,75	0,36%	$5 \cdot 10^{-15}$	100%	86%
Δt	min	10080	7,1	0,07%	$1 \cdot 10^{-16}$	4%	3%
p_{mean}	Pa	98981	50	0,05%	$1 \cdot 10^{-16}$	2%	2%
p_{actual}	Pa	101325	0	0%	0	0%	0%
δp_{mean}	Pa	0	50		$1 \cdot 10^{-16}$	2%	2%
δT_{mean}	K	0	0,01		$3 \cdot 10^{-16}$	6%	5%
w_{voc}	g/g	0,999	0,0006	0,06%	$1 \cdot 10^{-16}$	3%	2%
DR	$\mu\text{g}/\text{min}$	20,000	0,078	0,39%	$6 \cdot 10^{-15}$		

Table 5. Diffusion Rate Type A uncertainty calculation
Nominal DR 20 $\mu\text{g}/\text{min}$ over 1 week

Vial	1	2	3
x	23,520	22,275	23,983
u	0,051	0,052	0,051
u/x	0,22%	0,23%	0,21%

Table 6. Diffusion Rate Budget at INRIM conditions
Nominal DR 5 $\mu\text{g}/\text{min}$ over 4 weeks

X	[X]	x	u	u/x	$[c \cdot u]^2$	RI	AI
Δm	mg	206,60	0,75	0,36%	$3 \cdot 10^{-16}$	100%	89%
Δt	min	40320	7,1	0,07%	$8 \cdot 10^{-19}$	0%	0%
p_{mean}	Pa	98981	50	0,05%	$6 \cdot 10^{-18}$	2%	2%
p_{actual}	Pa	101325	0		0	0%	0%
δp_{mean}	Pa	0	50		$8 \cdot 10^{-18}$	2%	2%
δT_{mean}	K	0	0,01		$2 \cdot 10^{-17}$	6%	5%
w_{voc}	g/g	0,999	0,0006	0,06%	$8 \cdot 10^{-18}$	3%	2%
DR	$\mu\text{g}/\text{min}$	5,000	0,019	0,38%	$4 \cdot 10^{-16}$		

V. CONCLUSIONS

A VOC generator was designed following ISO 6145-8. Theoretical analysis of uncertainty showed the contribution of each combined variable. Temperature variability resulted to be the main contributor. Temperature control was enhanced to reach 0,01 K variability instead of 0,1 K considered by the norm.

Diffusion rate was measured weekly in different vials over 3 months period, in experimental conditions such that the INRIM and ISO uncertainty budgets can be compared. Type A uncertainty of measured values was compared with theoretical uncertainty calculated from combined variables uncertainty.

The enhancing of temperature control to reduce temperature variability of almost one order of magnitude was demonstrated to reduce theoretical diffusion rate uncertainty from around 0,8% to around 0,4% and Type A diffusion rate uncertainty from around 0,5% to around 0,25%.

Besides, with this reduced temperature variability, the use of a calibration balance at 0,5 mg (in respect to 0,05 mg) significantly influence the DR uncertainty (AI = 89%). Nevertheless the effect is mitigated by a reduced pressure variability.

VI. REFERENCES

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