Stability of standard dynamic VOC mixtures for atmospheric measures

A. Demichelis*, M. Sassi*, M. Lecuna*† and G. Sassi*†
*Istituto Nazionale di Ricerca Metrologica INRIM Torino, Italy
†Dipartimento di Scienza dei Materiali e Ingegneria Chimica Politecnico di Torino Torino, Italy
Email: a.demichelis@inrim.it

***Abstract*—Traceable and accurate standard of Volatile Organic Compounds VOC at trace concentration level are necessary for a framework of quality assurance and quality control of atmospheric composition measurements. Dynamic preparation of standard mixtures can fulfill the target accuracy given by the framework. Short-term concentration stability is one of the sources of uncertainty of dynamic preparation and depends on sampling time of the mixture, stability contribution to total uncertainty must be calculated. A method for the calculation of the stability contribution is here proposed. The performance of a preparation device for accurate VOC standard mixtures is here discussed as an application of the method. Two threshold values for stability contribution were set to consider the contribution negligible and relevant respectively. Experimental stability of the dynamic preparation device was measured. The stability of one of the five influence quantities resulted to give the total stability contribution. Stability contribution to total uncertainty resulted to be negligible below 60 min, while its contribution resulted to be relevant over 400 min.**

***Index Terms*—standard gas mixtures; VOC; concentration stability.**

I. INTRODUCTION

Traceable and accurate standard of VOC mixtures are necessary for a framework of quality assurance and quality control for the measurement of Volatile Organic Compounds (VOC) at trace concentration level in atmosphere, e.g., for the calibration of the gas monitoring stations of WMO-GAW network [1], Fig.1.

The framework determines an acceptable value of accuracy for the measurement first and for the standard mixture composition consequently. Accuracy was fixed for WMO-GAW network at 5% at ppb level as target expanded uncertainty for each VOC [2]. Currently the standards for WMO-GAW network are prepared in high pressure gas cylinders by several national metrology institutes [1] and they do not fulfil the requirements on target accuracy [1], [3].

Ongoing research programmes aimed to the WMO-GAW network target proposes static and dynamic methods for standard VOC mixtures preparation [1]. Both methods are linked to stability limits of VOC mixture composition, long term stability (years) for static methods [1], [3] and short term stability for dynamic methods [4]. Dynamics methods are the on time preparation of a standard mixture from a VOC source by dilution with a zero VOC gas, i.e., purified or synthetic air or nitrogen [5].

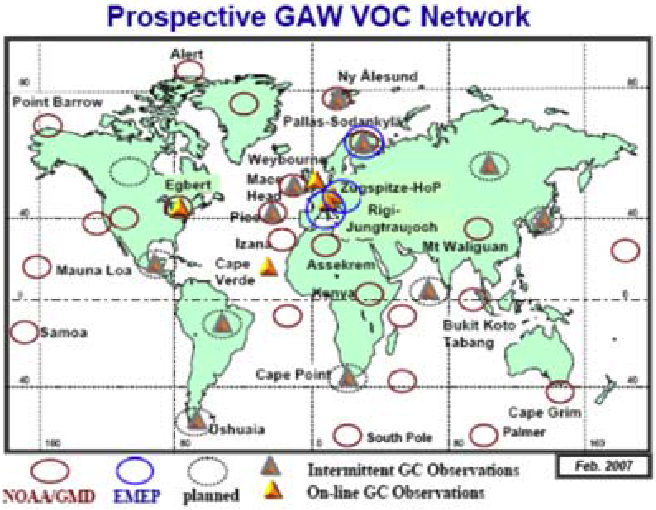

Fig. 1. WMO-GAW network for atmospheric composition measurement.

The concentration stability at a given observation time τ is defined by concentration fluctuations over the observation time. The observation time is the period over which the VOC mixture is prepared and sampled for analysis. Example of τ can be given by the charge duration of sorption tubes, the charging time of a cell, the sample time of a gas-chromatograph, the residence time of a flushing cell. The concentration stability influences the overall accuracy since it increases the concentration uncertainty due to sampling. VOC concentration stability depends on the fluctuations of the influence quantities and can be evaluated calculating data dispersion of the interesting quantity at different time scales. Allan deviation algorithm [6], commonly used in time and frequency metrology to analyze the stability behaviour of reference oscillators, can be employed to evaluate concentration stability at different time scales (observation times).

In dynamic methods, VOC mixture concentration is calculated from the influence quantities, i.e., generation rate and zero gas flow rates, thus mixture concentration stability depends on the stability of influence quantities. Uncertainty accounts for other sources generally negligible, i.e., wall adsorption effects, gas leakages from line-ups, mixing behaviours

[3], [7].

A method for the calculation of the stability contribution is here proposed. The performance of a preparation device for accurate VOC standard mixtures is here discussed as an application of the method. Two threshold values for stability contribution were set to consider the contribution negligible and relevant respectively. Experimental stability of the dynamic preparation device was measured.

II. EXPERIMENTAL

A. Mixture preparation device

The dynamic system device is the dilution in a single stage by purified air of a VOC flow rate generated by diffusion. Referring to Figure 2, a purified air flow rate (ϕ_1 of 10 – 25 l/min at standard conditions) is mixed with the VOC diffusion rate (D_R of 0.1 – 1ug/min) carried by purified air flow rate (ϕ_C around 50 ml/min at standard conditions). Purified air is controlled in pressure (PR-1) and temperature (TC-1) to regulate flow rates (ϕ_1 and ϕ_C) across sonic nozzles, while liquid VOC and diffusion pipe are controlled in temperature (TC-2) to regulate diffusion rate D_R. Generation pressure (p_G of 45-800 Pa as relative pressure) is regulated by a valve (PR-2) at the end of dilutor line. The following instruments were used to control operative quantities: pressure reducer (model Tescom 44-2200– 7 bar.g.) for PR-1, a gate valve for PR-2, laboratory air conditioning at 0.1 K for TC-1, thermostatic bath (model HAAKE DL30-W46/B Heating Open Bath Circulator) for TC-2. VOC concentration in the mixtures (χ_{VOC}) in the range of 1 – 100 ppb$_{mol}$ can be generated by the device; acetone was assumed as VOC model for calculations.

B. Measurement and calculation of stability

Air absolute pressure (p_A) and temperature (T_A), generation absolute pressure (p_G) and temperature (T_G) are recorded, as reported in Fig. 1. The following instruments were used to record operative quantities: absolute capacitance manometer (model MKS Baratron 722B – 5000 torr) for p_A with a 0.5% calibration accuracy, pressure meter (MKS Baratron Type 310BHS-1Pressure Head – 1000 torr) for p_G with a 58 Pa calibration accuracy, temperature meter (industrial Pt100) for T_A with a 0.02 K calibration accuracy and temperature meter (Minco Pt100) for T_G. Temperature and pressure data were acquired over 3 days every 30 seconds at a nominal VOC mixture preparation of 30 ppb by mol. Stability of quantities were calculated with Allan algorithm in an observation time range of 1 to 1000 minutes.

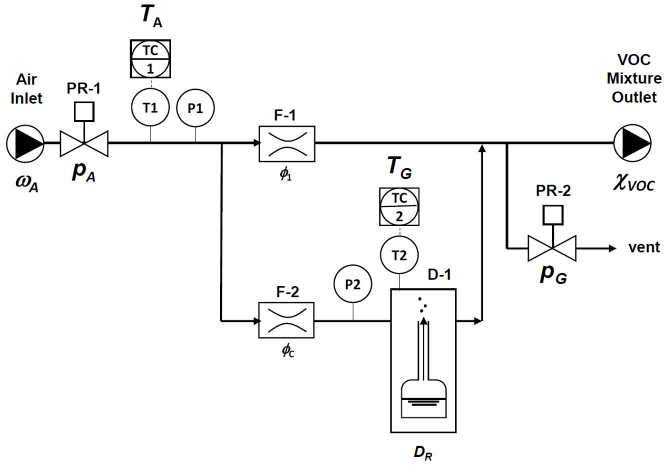

Fig. 2. Scheme of the dynamic device for prepration of reference VOC mixture. PR-1 and PR-2: pressure reducers. TC-1 and TC-2: temperature controllers. F-1, F-2 and D-1: flow rate controllers. P1 and P2: absolute pressure sensors. T1 and T2: temperature sensors.

III. MODEL FOR VOC CONCENTRATION STABILITY

VOC concentration χ_{VOC} is calculated with the following equation (eq. 1).

$$\chi_{VOC} = \frac{MW_A}{MW_{VOC}} \left[\frac{D_R + \omega_A(\phi_C + \phi_1)}{(\phi_C + \phi_1)} \right] \qquad (1)$$

In which ϕ_1 depends on p_A and T_A by the sonic flow model [8] and D_R depends on T_G, and p_G by the gravimetric model [3], ω_A is the air purity toward the generated VOC. Stability is an uncertainty source and can be treated as other sources. Measurand stability depends on operative stability of the device. Operative quantities for the considered device are: T_A, p_A, T_G, p_G, ω_A. The quantities T_A, p_A, T_G have a control system, ω_A depends on external device, i.e., an air purification system, p_G is regulated by a valve and depend on atmospheric pressure. From the model obtained by substitution of operative equations [3], [8] in the balance equation (eq. 1) sensitivity coefficients, as first derivative of the model in respect to operative quantities, can be calculated by definition [9].

IV. TARGET STABILITY OF DYNAMIC REFERENCE VOC MIXTURES

The device operates at set point values of controlled quantities, at target value of air purity and at absolute pressure that depends on atmospheric pressure in the reference time. Mean value of VOC concentration prepared in the reference time results from the mean value of operative quantities in the same reference time. The stability of operative quantities depends on duration of reference time, on control systems, on atmospheric pressure stability on the performances of air purification system. The stability of combined quantities, as the VOC concentration, is calculated from the stability of operative quantities [9]. The contribution of each quantity to the total VOC concentration uncertainty is calculated as quadratic product of operative quantity stability and its sensitivity coefficient to VOC concentration. The contribution of the VOC concentration stability to total VOC concentration uncertainty is the sum of the contributions of all operative quantities. The device and its control systems can be designed with a target stability that comes from the limitation of the stability contribution to the total VOC concentration uncertainty. The stability contribution is negligible when it is lower than 1% of total concentration uncertainty, while it is surely relevant

X	[X]	$\bar{x}$	$\sigma_{T,i,1\%}$		$\sigma_{T,i,10\%}$	
			[X]	%	[X]	%
ω_A	ppb mol	0.096	0.06	60	0.18	190
T_G	K	299.15	0.009	0.003	0.029	0.010
p_G	Pa	98500	36	0.036	110	0.12
T_A	K	293.15	0.26	0.090	0.83	0.28
p_A	Pa	270000	120	0.046	390	0.14
χ_{VOC}	ppb mol	30	0.03	0.1	0.09	0.3

TABLE I
STABILITY BUDGET OF VOC CONCENTRATION. $u_T(\chi_{VOC}) = 1\%$

when it is higher than 10%. Following the ISO Guide [9], the target concentration stability $\sigma_{T,\chi}$ is calculated as a fraction of total VOC concentration uncertainty:

$$\sigma_{T,\chi} = \sqrt{I_{S,T}} \cdot u_T(\chi_{VOC}) \tag{2}$$

In which $u_T(\chi_{VOC}$ is the target total VOC concentration uncertainty, $I_{S,T}$ is the target significance index of concentration stability contribution, i.e., 1% for a negligible contribution and 10% for a relevant contribution.

In the hypothesis of equal contribution, the target stability for each quantity $\sigma_{T,i}$ is thus calculated as:

$$\sigma_{T,i} = \sqrt{\frac{I_{S,T}}{N}} \cdot \frac{u_T(\chi_{VOC})}{c_{i,\chi}} \tag{3}$$

In which $c_{i,\chi}$ is the sensitivity coefficient of VOC concentration in respect to i-th operative quantity, N is the number of operative quantities. The preparation of a VOC concentration at 30 ppb by mol using the considered device has a total uncertainty of 1% k=1 [7]. In table I, mean values $\bar{x}$ and target stability values for each operative quantity are reported for a negligible $\sigma_{T,i,1\%}$ and for a relevant contribution $\sigma_{T,i,10\%}$ to the total concentration uncertainty, both as absolute and relative values. The mean and target stability values for VOC concentration stability are also reported, in the last row.

V. EXPERIMENTAL STABILITY OF DYNAMIC REFERENCE VOC MIXTURES

Figure 3 shows the stability results calculated with the Allan algorithm over the acquired experimental data for each operative quantity. Data are relative to the quantity mean value and are reported for observation times of 1 – 1000 min.

All stabilities increase with observation time, 0.7 was calculated as a slope for p_A, p_G, T_A, while 0.3 was calculated for T_G. The more stable and less time dependent quantity is T_G; pressure terms are less stable than temperature terms; the less stable quantity is the pressure of the air dilution flow rate p_A.

The experimental significance $I_{S,exp,i}$ of each operative quantity to the total experimental uncertainty obtained $u_{exp}(\chi_{VOC}, \tau)$ for the prepared VOC mixture concentration can be evaluated as:

$$I_{S,exp,i} = \left(\frac{\sigma_{exp,i}(\tau) \cdot c_{i,\chi}}{u_{exp}(\chi_{VOC}, \tau)} \right)^2 \tag{4}$$

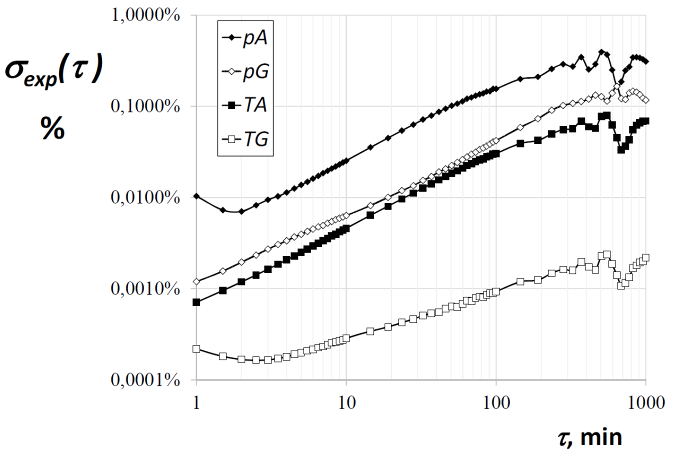

Fig. 3. Experimental stabilities of operative quantities, calculated with relative Allan deviation at different observation times.

Figure 4 shows the significance obtained for each operative quantity calculated in the observation time range defined by Allan deviation calculation.

The experimental p_A stability, among the other operative quantity, gives the greatest contribution to concentration stability and, in turn, to total VOC concentration uncertainty.

The sum of stability contribution for all operative quantity, i.e., the concentration stability contribution, almost coincides with the p_A behaviour, which gives the main contribution.

For mixture observation time lower than 6 min, e.g., sampling in a gas chromatograph for instrument calibration and analysis, no stability of any quantity of the primary generator device can be considered as uncertainty source to prepared VOC concentration. For mixture observation times between 6 and 60 min, e.g., loading of sorption tubes for VOC reference material preparation, stability contribution is negligible. For mixture observation time higher than 60 min, e.g., filling of a canister for long-term exposure measurement, pressure stability should be considered to calculate concentration uncertainty.

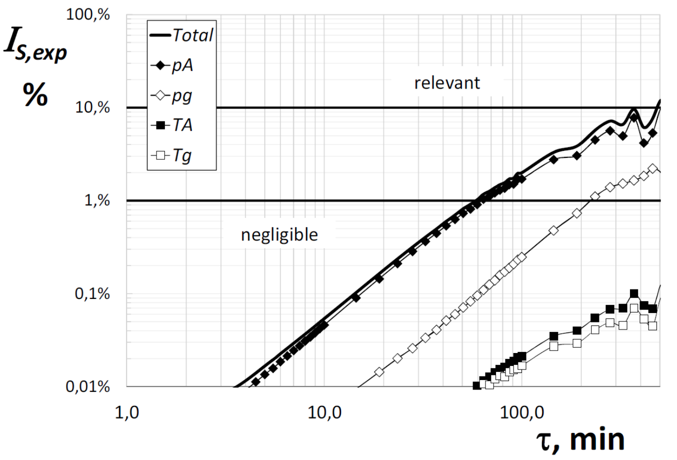

Fig. 4. Analysis of the experimental significance, to total VOC concentration uncertainty, of operative quantities stability, in function of observation time.

VI. CONCLUSION

A method for the realization of accurate reference VOC concentration at ppb level is presented. An experimental device is build up and a model for VOC concentration stability is redacted. Target stability of operative quantities to give a negligible and relevant contribution to total VOC concentration uncertainty at 1% are calculated obtaining negligible target stability lower than 0.05% for pressure terms, 0.003% for temperature stability of dynamic source and 0.09% for temperature stability of dilution air flow rate.

Allan deviation calculations are applied to experimental stability data of operative quantities to evaluate the experimental stability of the VOC mixture generator device. Stability behaviour highly time dependent are found for some quantities, the stability of pressure of dilution air flow rate give the main contribution to the concentration stability.

Significance of experimental obtained stabilities are calculated resulting in negligible stability contributions to total VOC concentration uncertainty for mixture sampling time lower than 6 min. For mixture observation time higher than 60 min, pressure stability should be considered to calculate concentration uncertainty since it will give a relevant contribution.

This work helps is defining mixture observation time needed to realize the best accuracy in preparation of reference VOC mixture at ppb level for atmospheric and environmental measurements purposes.

VII. ACKNOWLEDGMENT

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