METAS

Dynamic generation of VOCs reference gas mixtures with a mobile generator and comparison to static preparations

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Abstract

Several volatile organic compounds (VOCs) are known to be very reactive. The production of reference gas mixtures at very low level, typically nmol/mol, has to face the challenges of VOCs adsorption and reaction with material surfaces. As a solution, METAS built a coated reference gas mixture generator «ReGaS2» based on permeation and dynamic dilution. It generates up to 5 volatile organic compounds at trace level (nmol/mol) simultaneously. ReGaS2 was used during ENV56 KEY-VOCS for a comparison for Ethanol and Methyl Vinyl Ketone with VSL. VSL developed reference gas mixtures containing trace amount fractions of several oxygenated VOCs by gravimetric method and using novel cylinder treatments. The reference gas mixtures were in agreement within their uncertainties confirming the progresses made by using dynamic methods and novel coatings. Later on, ReGaS2 was used on site at Hohenpeissenberg (Meteorological Observatory of DWD) to generate mixtures of several VOCs in order to calibrate their measuring device routinely used for atmospheric measurements.

Development: Design of ReGaS2

ReGaS2 is a mobile SI-traceable reference gas generator [1]. It generates gas mixture of several volatile organic compounds at ambient level (nmol/mol). It has the following characteristics:

→ 1 MassFlowMeter + 2 MassFlowControllers

→ Pressure and Temperature regulated

→ Pre-heated inlet gas

→ Temperature measurement in the chamber

→ Output flow 1-6 L/min

→ 1 to 5 compounds generated simultaneously (see Fig. 2)

→ SilcoNert® 2000 coating to reduce adsorption

→ Reproducibility of gas mixture < 1.5%

→ Uncertainty of gas mixture < 4% (k=2)

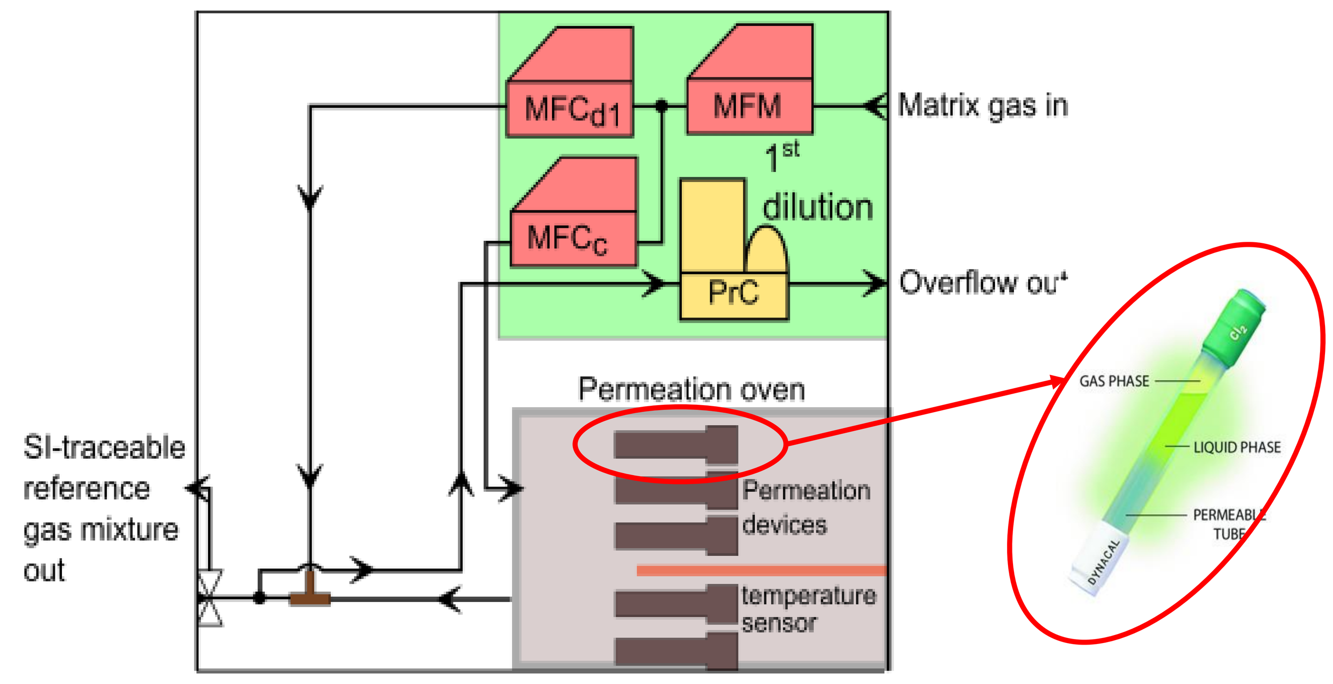


Figure 1: Design of the mobile SI-traceable reference gas generator «ReGaS2». On the right-hand side, as example for the permeation device, a sketch of a typical tubular permeator.

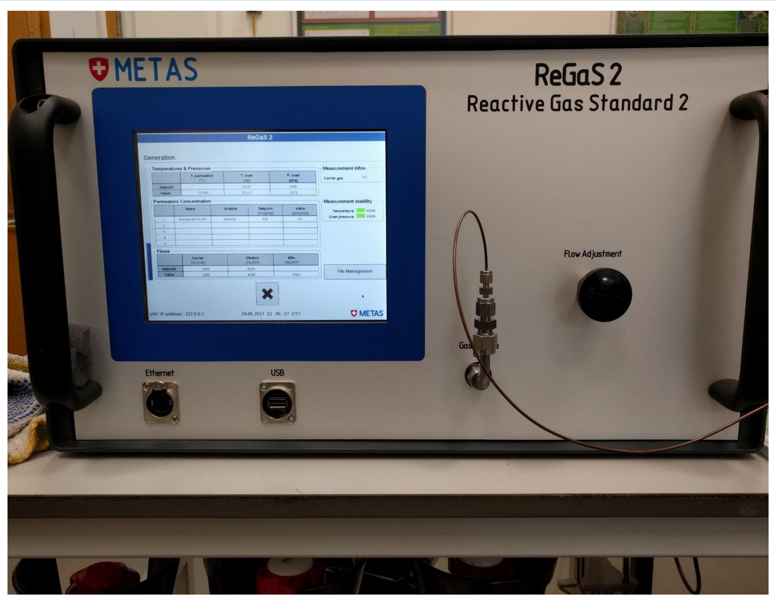


Figure 3: Picture of ReGaS2 front panel. The user-friendly software was developed in-house.

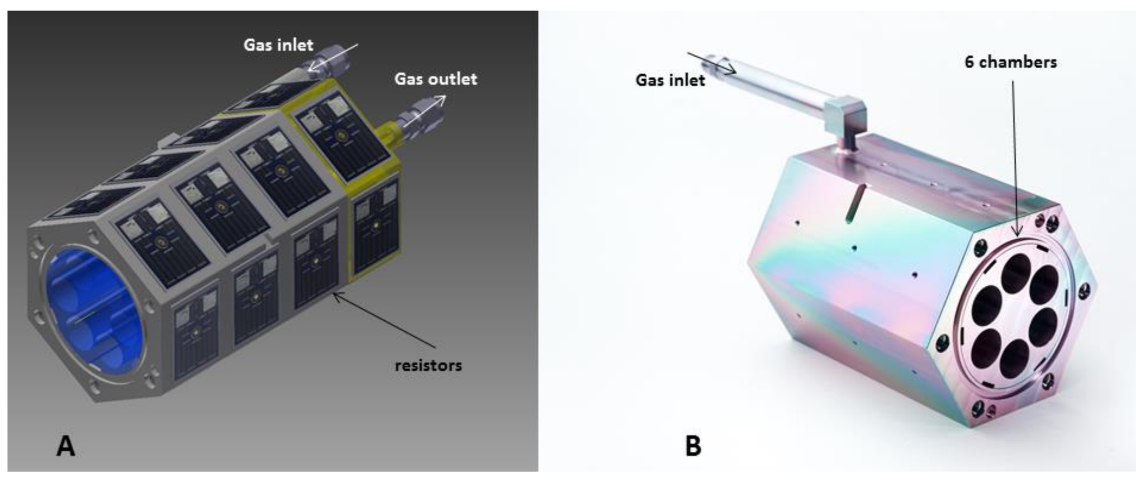


Figure 2: Computer-Aided Design (A) and picture (B) of the in-house developed oven of ReGaS2 with 6 permeation chambers. One chamber is reserved for the internal temperature sensor. The oven is entirely coated with SilcoNert®2000.

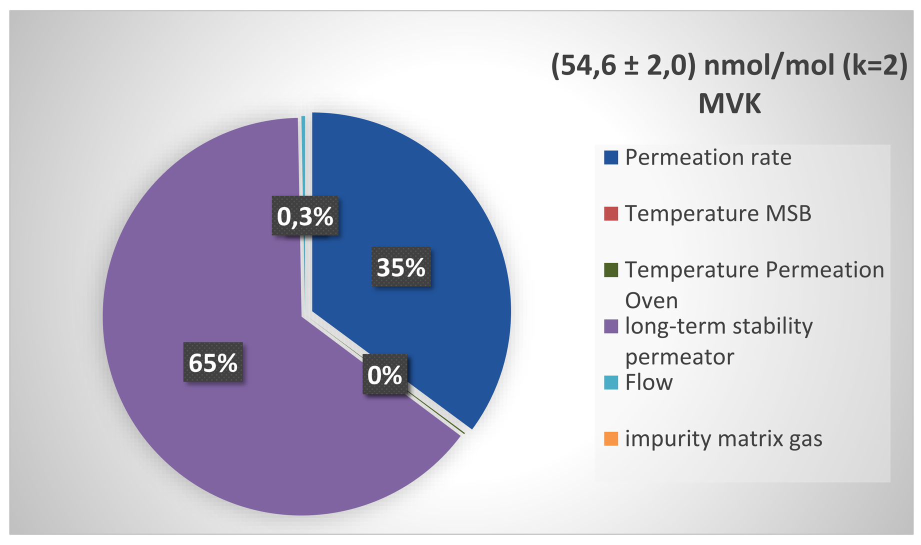
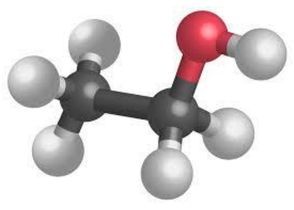


Figure 4: Uncertainty budget for the generation of circa 54 nmol/mol methyl vinyl ketone (MVK) with the ReGaS2 during several days. The main contributions to the uncertainty come from the permeation rate determination and its long-term stability.

Validation : Comparison dynamic-static mixtures

A comparison was conducted to compare progresses in the realisation of VOCs reference gas mixture [2]. At VSL, ReGaS2 generated a mixture of ethanol and methyl vinyl ketone at the nmol/mol level in nitrogen. VSL measured the mixture coming out of ReGaS2 and compared it to their reference gas mixtures in coated stainless steel cylinders. The oxygenated VOCs were measured with a Thermal Desorption (TD)-GC-FID system.



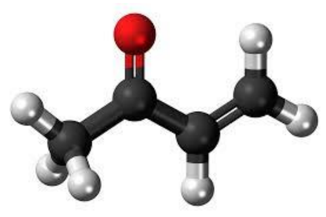


Figure 5: Picture of novel coated stainless steel cylinder used for preparation of VSL reference gas mixtures.

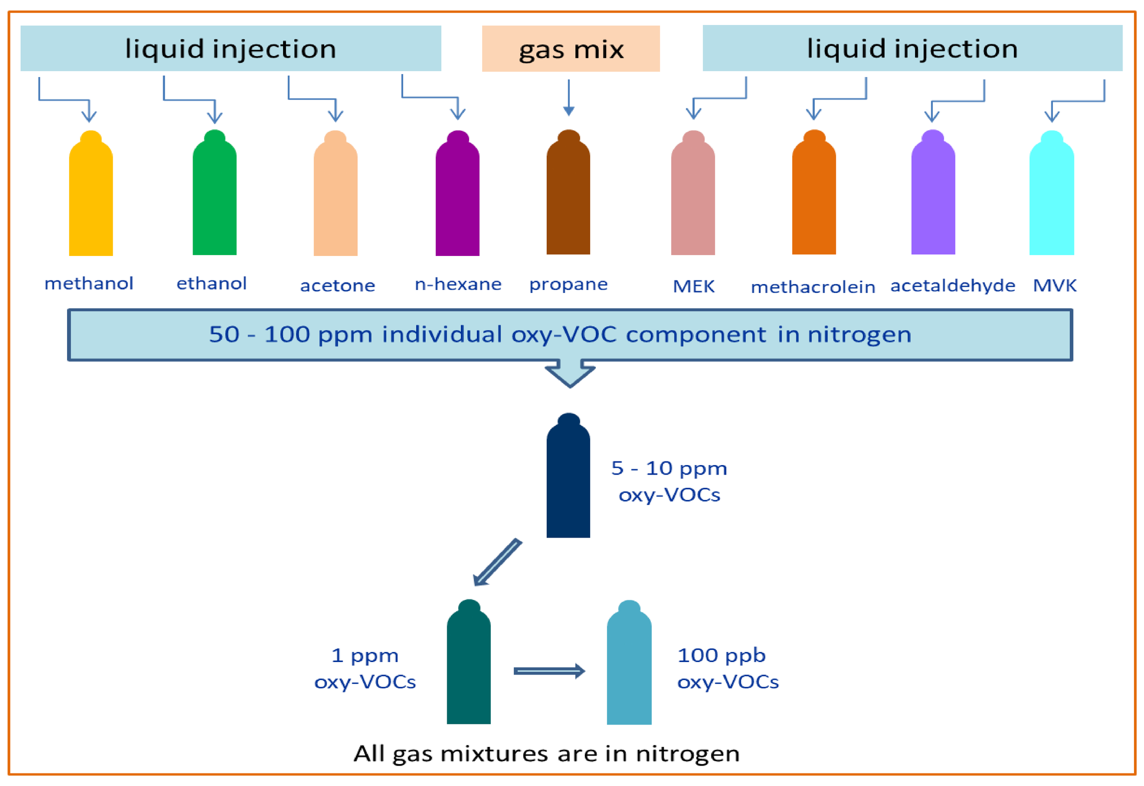


Figure 6: Preparation scheme of VSL reference gas mixtures for oxygenated VOCs. Preparation method: gravimetric according to ISO 6142-1:2015.

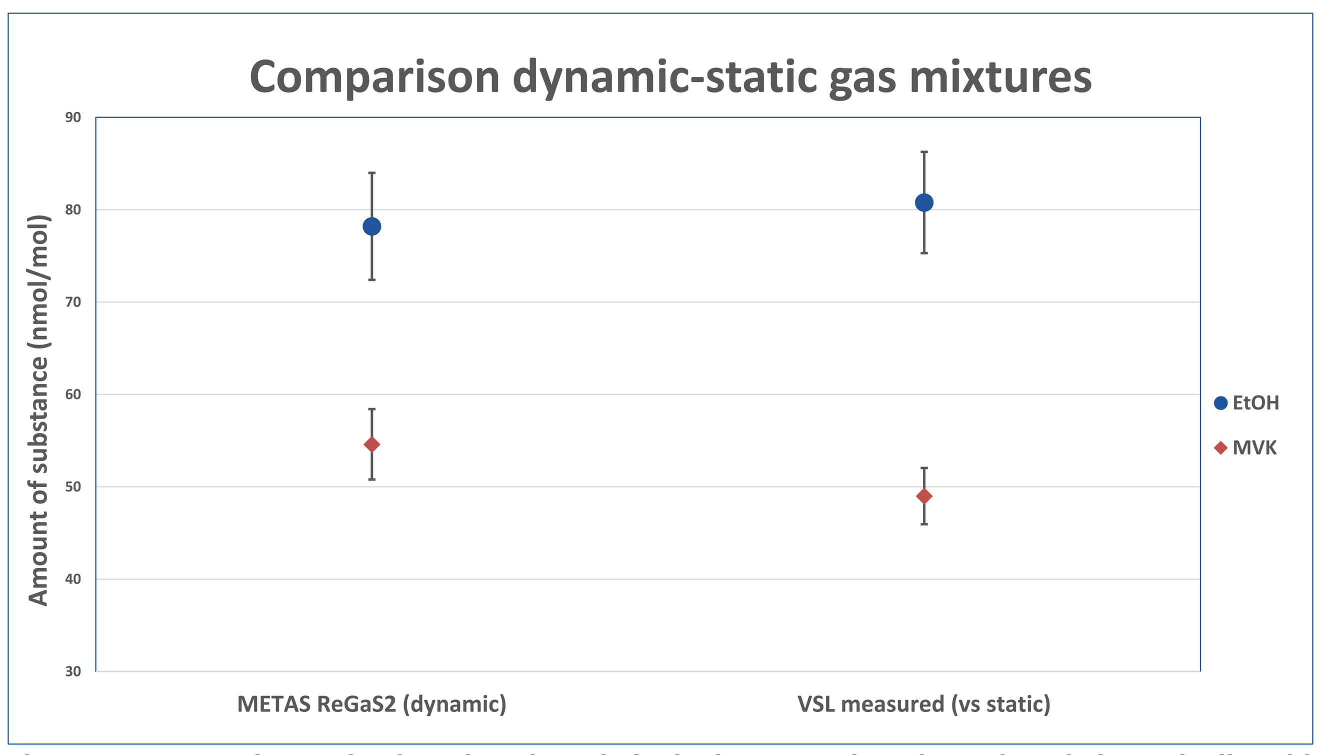


Figure 7: Comparison of Ethanol and Methyl Vinyl Ketone (MVK) produced dynamically with ReGaS2 (METAS) and gravimetrically in novel cylinders (VSL). The blue and red dots are the amount of substance fraction of Ethanol and MVK respectively. Error bars represent uncertainties (k=2)

The dynamic generation of Ethanol and MVK with ReGaS2 is in agreement with the novel gravimetric production of static mixtures.

The coating minimizes the adsorption of reactive compounds and therefore improves the stability of the reference gas mixtures at low levels.

Utilisation : Generation of VOCs on site

The ReGaS2 was sent to Meteorological Observatory Hohenpeissenberg (MOHp) to produce a mixture of terpenes in nitrogen (sabinene, terpinolene, β-phellandrene, β-pinene, limonene). The mixture was used to calibrate and check the stability of their GC-FID/MS system.

Figure 8: Panorama at MOHp [3]. This GAW (Global Atmosphere Watch) Global station is also part of the ACTRIS network

VOCs are measured at MOHp with a GC-FID/MS system with a custom-made pre-concentration unit (Fig. 9). For the ReGaS2 analysis mole fractions were derived from FID results applying the average C-response factor for terpenes based on a calibration with a NPL standard gas mixture (with 10 monoterpenes).

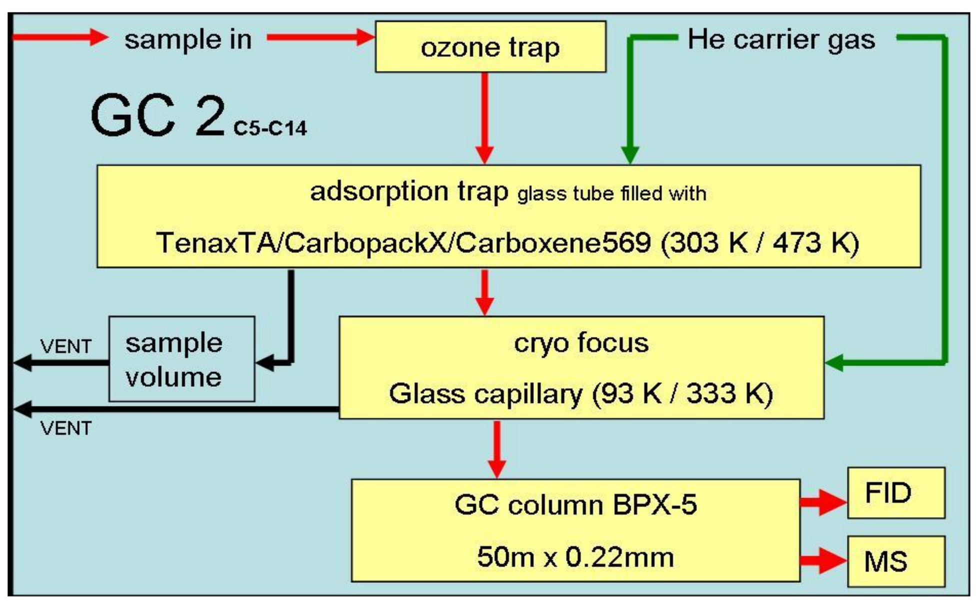
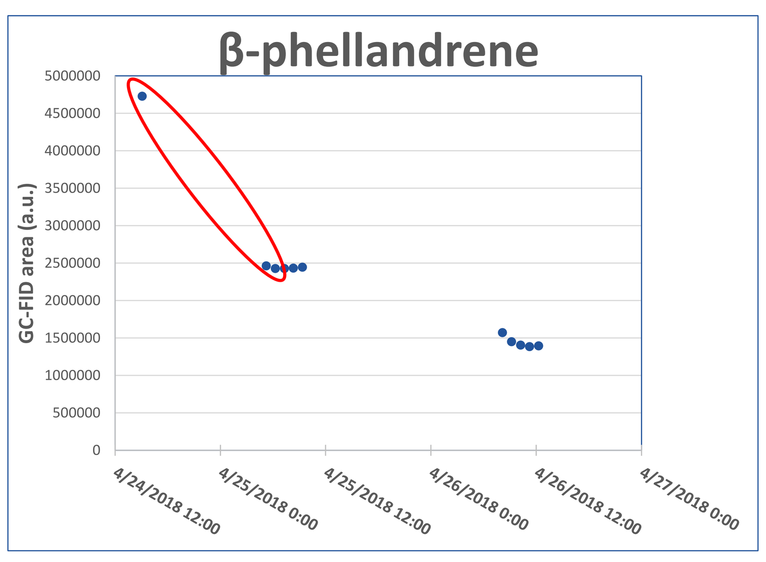


Figure 9: Schematic of the MOHp GC-FID/MS system for biogenic VOCs



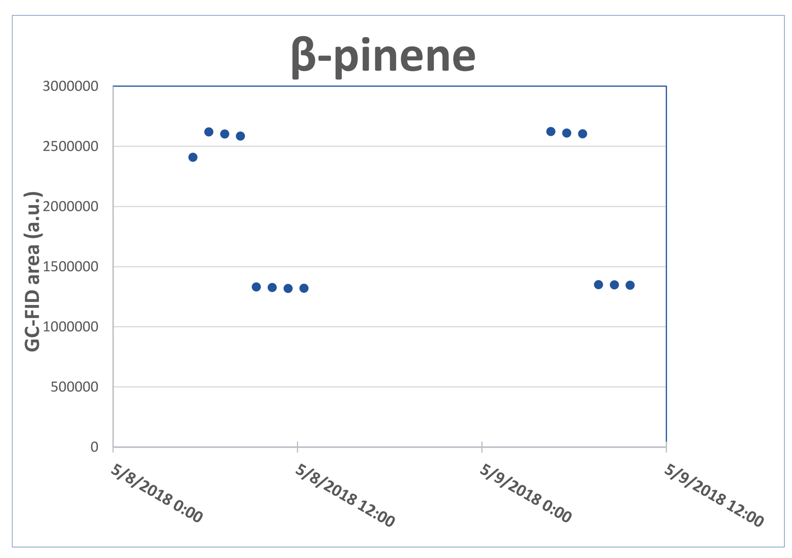


Figure 10 and 11: Measurements of β-phellandrene and β-pinene with GC-FID generated with ReGaS2 at 2 different concentrations by changing the dilution flow. Figure 10 : 10 – 7 nmol/mol of β-phellandrene . Figure 11 : 50 - 30 - 50 - 30 nmol/mol of β-pinene. The red circle shows the stabilisation periode of the permeator.

After a typical stabilisation period of 1 to 3 days for the permeation rate, the stability of the measured concentration is better than 1 % and the reproducibility (see Fig. 11) is better than 2 %. Investigations on the long-term reproducibility (e.g. months) of the permeation rate are still ongoing.

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KEY-VOCs DWD VSL

References
(1) Pascale et al., *Two generators to produce SI-traceable reference gas mixtures for reactive compounds at atmospheric levels*, Measurement Science and Technology, 2017
(2) Baldan A, *Final Publishable JRP Report KEY-VOCS* (https://www.key-vocs.eu/), consulted 08.03.19
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