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1 Executive Summary

Introduction

Volatile Organic Compounds or VOCs are organic compounds or chemicals that contain carbon and easily become vapours or gases. They are found in many products commonly used every day. Some VOCs are dangerous to human health whilst others cause harm to the environment by influencing the oxidative capacity of the atmosphere, contributing to the production of other air pollutants as well as to greenhouse gases and ozone, and by being also involved in the formation of secondary organic aerosols. These VOCs are regulated by European legislation.

This project improved the measurement infrastructure for key VOCs in air by providing traceable and comparable reference gas standards and by validating new sensor-based measurement systems in support of the air monitoring networks and the EU regulations.

The Problem

VOCs are released from burning fuel, and emitted from oil and gas fields and diesel exhaust. They are also released from solvents, paints, glues and other products that are used and stored at home and at work.

Some of the VOCs which pose a threat to environment, climate and health are regulated by EU legislation. Sampling and analytical methods of trace level, part-per-billion (ppm) to part-per-trillion (ppt), VOCs in air were available before this project but they suffered from the fact that the majority of VOCs will stick on surfaces or react with other species during measurement. For those reasons, accuracy in VOC measurement results was still a challenge and the availability of suitable traceable standards was limited. New emerging sensing technologies had the potential to replace standard techniques, but they needed to be properly validated.

The Solution

This project developed methodologies to quantify losses of VOC trace gases, due to adsorption on material surfaces, and demonstrated the suitability of specific novel coating technologies.

In addition, the gained capability of measuring at ultralow levels (few part-per-trillion) allowed the quantification of interfering VOC impurities present in clean nitrogen or air used in instrument calibration.

For the first time, standard gas mixtures in cylinders and portable calibrators able to deliver trace concentration levels of a priority list of anthropogenic (oxygenated-VOCs) and biogenic (monoterpenes) VOCs are available for atmospheric monitoring. It must be noted that it was also demonstrated that for some very reactive VOCs, such as formaldehyde, instability remain an issue and that further research and other coating technologies are needed to be able to provide suitable gas standards.

Reference materials and transfer standards are now ready for a set of polar- and semi-VOCs, particularly important in emission testing of construction products.

Impact

This project has set a major step in addressing the importance of interaction of VOCs on contact surfaces and has demonstrated that VOCs are heterogeneous and therefore they behave differently when sampled, analysed and stored. In the longer-term it is expected that coating industry will make use of the project findings and methodologies and will work at the development of new passivation technologies to produce inert materials, so that even the most reactive and unstable VOCs can be finally quantified beyond all doubt. Several World Meteorological Organization Global Atmosphere Watch (WMO GAW) stations, responsible for the measurement of VOC trends in atmosphere, are currently using gas standards developed in this project for a round-robin exercise. In addition to that, the project's outputs, such as the verification of zero gases, have been included in the WMO guideline for Non-Methane Hydrocarbons. In the long-term it is expected that all GAW station (worldwide) will meet the challenging Data Quality Objectives for the key VOCs they need to monitor and therefore they will provide accurate measurement of VOC trends needed in climate change research.

The two portable calibrators (dynamic gas generators), developed in this project, have been applied for the calibration of instrumentation in the field for both air monitoring and health applications (breath analysis). These prototypes have the advantage to be flexible in the generation of gas concentrations and, if proven to be robust and easy to use, they will be a valid option for use in the field. An interesting spin off, the ReGas2 portable generator will be commercialised in the short-term future.

The validation protocol for gas sensors developed in this project has fed the drafting of the Technical Specifications "Air quality – Performance evaluation of air quality sensors" by CEN/TC264/WG12. In addition, the results of the gas sensors evaluation have helped decision makers understand the benefits and limitations of these sensor devices when applied in the field. It is estimated that in the longer term, improved sensing technologies will impact the implementation of the Air Quality Directive and more widely the way we will perform VOC measurements, independent of the application.

2 Project context, rationale and objectives

The broad class of Volatile Organic Compounds (VOCs) includes several species dangerous for human health and for environment. Some of them are regulated in EU legislation, such as benzene in the Air Quality Directive (2008/50/EC) and other hazardous VOCs in the Construction Products Directive (89/106/EEC) and subsequent Construction Products Regulation (305/2011/EU, CPR). VOCs are also reactive components, responsible for the formation of ozone and secondary pollutants in the atmosphere and therefore contributing to climate change. The trends of VOC species and their concentration levels, even if in trace amounts, need to be accurately measured.

Three networks are actively involved in the measurement of VOCs in air: the atmospheric monitoring, the ambient air and the indoor air quality networks.

The World Meteorological Organization (WMO), Global Atmosphere Watch (GAW), is the atmospheric monitoring network operating at global scale. This network is responsible for the measurement of trends of VOCs and other species, like green-house gases, in the atmosphere. GAW stations are located at remote sites, such as the Jungfraujoch in Switzerland at ca. 3500 m height, so that they can measure background levels without being affected by emissions due to human activities. The presence of VOCs is at few part-per-billion (ppb) down to part-per-trillion (ppt) levels. The challenges at these extreme low levels are then the ability of sampling and measuring accurately.

At European level, the EU research infrastructure project ACTRIS aims, among other activities, at demonstrating the compliance of VOC measurement results carried out by the EMEP and WMO/GAW stations, members of the project, with specific challenging Data Quality Objectives (DQOs). As example, the measurement uncertainty DQOs for oxygenated-VOC and monoterpenes are set to 10 %, half of the values defined by the WMO/GAW network.

The KEY-VOCs project replied to the need of the atmospheric monitoring network to have calibration standards with specific accuracy and long-term stability for a selection of key VOCs. Unfortunately, due to their physical and chemical properties, these species are prone to adsorb or react on contact with material surfaces, causing a loss of VOC in gas phase. These effects are therefore significantly affecting both the development of certified reference materials (gas mixtures with accurate composition in compressed gas cylinders) and the measurement of these components in air. In addition, another critical issue is the reliability of the zero gas (clean nitrogen or clean air) used for zero calibration and dilution gas. The 'undetected' presence of even a few tenths of a part-per-trillion of VOCs in the zero gas will cause a significant error when measuring at such extreme low levels.

The scientific and technical objectives of the project were:

The project objectives were:

1. Adsorption and reaction effects on surface materials and zero gas standards

- Quantitative study of the adsorption and reaction effects of VOCs on surface materials in order to find the best suitable materials and passivation techniques when measuring at trace levels. Tested surfaces include the sampling lines, pressurised vessels, pressure regulators and dilution systems.

- Develop traceable standards for VOC-free zero gas (both air and nitrogen). This objective includes the efficiency of purification technologies in removing VOC impurities at part-per-trillion trace level concentrations (ppt).
- Mathematical tools for calculating the uncertainty contribution of adsorption and reaction phenomena in sampling and dilution lines as well as for the gas treatment.

2. Reference standards to underpin atmospheric monitoring of VOCs

- Develop traceable, accurate and long term stable gaseous reference standards of key VOCs which play a key role in the chemistry of the atmosphere affecting climate and air quality by a static preparation method. Such standards include oxygenated-VOCs (OVOCs), formaldehyde and monoterpenes at part-per-million (ppm) and part-per-billion (ppb) level.
- Develop traceable and accurate gaseous reference standards of key VOCs which play a key role in the chemistry of the atmosphere affecting climate and air quality by dynamic generation methods. Such standards include oxygenated-VOCs and formaldehyde at ppb levels.
- Validate the developed measurement gas standards by organisation of a comparison among the project partners

3. Development of gas standards to underpin Indoor air measurements

- Develop reference gas standards for key polar and semi-VOCs for indoor air QA/QC activities.
- Develop constant emitting polymer materials for the quality control of emissions testing procedures (e.g. emission test chamber method).
- Validate the developed measurement gas standards by organisation of a comparison among the project partners

4. Validation of measurement standards and measurement systems

- Validate measurement systems (sensors and portable devices) commercially available for the measurement of VOCs. The work includes the review of the existing measurement systems, the development of a testing protocol and calibration procedures and the laboratory and field validation. The target VOCs are the aromatics, in particular benzene as it is regulated by law.

3 Research results

3.1 Adsorption and reaction effects on surface materials and zero gas standards

3.1.1 Quantitative study of the adsorption and reaction effects of VOCs on surface materials

VOC vapours are known to be prone to adsorb on contact surfaces, such as those used for gas standard preparation, sample storage, transport and analysis. Among various VOCs, the measurement of oxygenated VOCs (OVOCs), like methanol and ethanol, is very challenging as these gases strongly interact with various metal surfaces including stainless steel (found in e.g., sampling lines or pressure regulators) and aluminium (e.g., gas cylinders). The lower the OVOC mole fraction that needs to be obtained as standards or measured in air, the more important it is to use suitable materials to minimise the adsorption effect on the material and therefore the loss of component in gas phase. The interaction of methanol and other OVOCs has been investigated at static and dynamic conditions with the aim to improve respectively the preparation of (long-term stability) gas standards in pressurised cylinders and to guarantee the integrity of the real air samples during sampling.

VOC adsorption on cylinder surfaces

The first part of the research consisted of quantitatively study the adsorption of VOC at trace levels for a selection of different aluminium and stainless steel pressurised cylinders having proprietary passivation treatments. A batch of gas mixtures containing several OVOCs, including methanol, ethanol and acetone, at 100 nmol/mol, a batch containing formaldehyde (F) at 1 µmol/mol and a batch containing several

monoterpenes (MT) at 2 nmol/mol have been prepared using state-of-the-art gravimetric preparation methods (ISO 6142-1).

Four batches of gas cylinders were supplied for testing by specialty gas producers (Takachiho, Air Liquide, Air Products, and Linde, hereafter referred to as cylinders A – D randomly indicated to protect the anonymity of the provider). The list is shown in Table 1.

Table 1: List of selected passivated cylinders for the decanting study

Cylinder type	Application	Cylinder volume
A	OVOC/F	Aluminum / 10 L
B	OVOC/F	Aluminum / 10 L
C	OVOC/F	Aluminum / 10 L
D	OVOC/F	Aluminum / 10 L
SW (Swagelok)	OVOC	SS Sulfinert Coated / 3.6 L
Spectra Seal (BOC/Linde)	MT	Aluminum / 10 L
Experis VOC (Air Products)	MT	Aluminum / 10 L

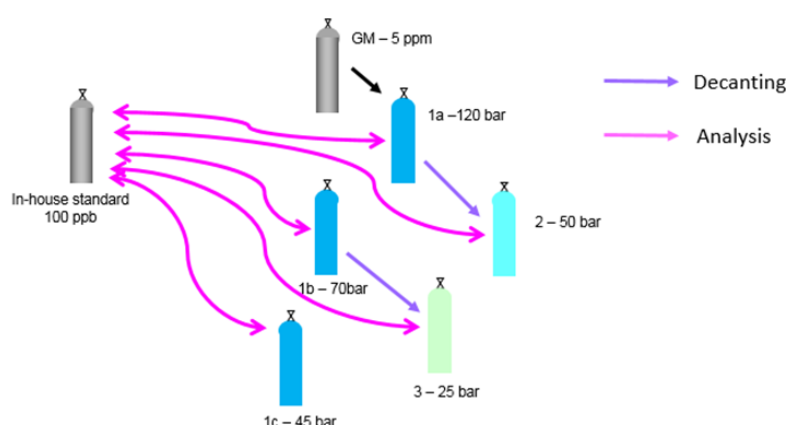


Figure 1: Panel A (left) Decanting procedure performed for the OVOC for each cylinder type at NPL (blue cylinder is the mother, light blue and green are the daughter decanted cylinders). **Panel B (right)** Decanting set-up at VSL

Losses occurring upon gas mixture preparation have been quantified by decanting method. According to this method, freshly prepared gas mixtures in cylinders are poured by pressure difference into identical empty and clean cylinders. Provided this method is applied in a controlled way, the measured difference in composition between the “mother” and “daughter” indicates the loss of VOC and therefore the degree of adsorption of the VOC on the cylinder surface. An example of decanting protocol for OVOC is depicted

in



Figure 1, while Figure 2 shows the results of one decanting experiment for formaldehyde in cylinder type D. The decanting protocol was run twice for the same cylinder type.

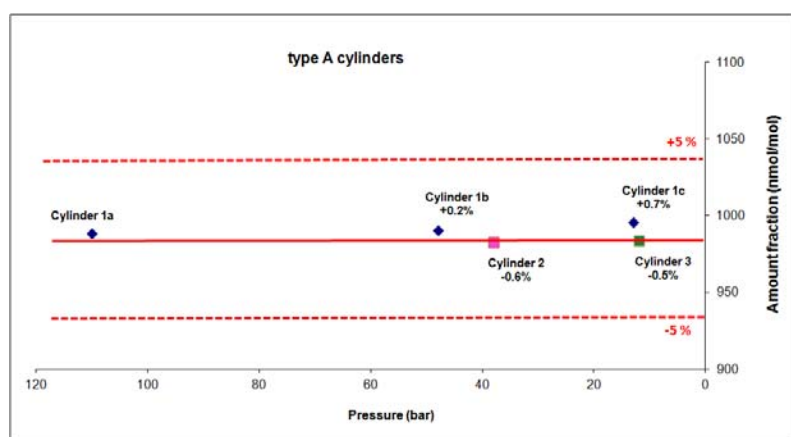


Figure 2: Results for decanting test performed for formaldehyde on cylinder type A at LNE

Table 2 and Table 3 give the representation of the results of the testing. When the decanting effect (deviation of the concentrations of the daughter cylinder/mixture from the mother cylinder/mixture) is within 5%, the symbol “+” is used. This symbol indicates that the type of cylinder is **suitable** for the component; when the decanting effect is between 5% and 10%, the symbol “-” is used. This symbol indicates that the type of cylinder is **less suitable**. When the decanting effect is above 10%, the symbol “—” is used. This symbol indicates that the type of cylinder is **not suitable** for the tested component. The symbol “(-)” means that the effect is close to “less suitable”, and the symbol “(+)” close to “suitable”.

Table 2: Decanting results for OVOC and formaldehyde on each type of cylinder tested. Note that for type D* cylinders for formaldehyde differ from those for OVOC

Cylinder type	A	B	C	D*	SW
Formaldehyde	(-)	+	-	+	
Methanol	—	-	—	—	-
Ethanol	-	+	—	—	(+)
Acetone	+	+	+	+	+
Methacrolein	+	+	+	+	+
MVK	+	+	+	+	+
MEK	+	+	-	-	+

Table 3: Decanting results for MT on each type of cylinder tested

Cylinder type	Experis VOC	Spectra Seal
n-octane	+	+
+/- α -pinene	+	—
+3-carene	+	—
Limonene	+	—
1,8-cineole	+	—

Based on the results obtained with this study, the best performing cylinder types were further used for the development of the gas standards for atmospheric monitoring.

For OVOC, cylinder types B and SW show the best performance. While type B cylinder is made of aluminium, the SW is a stainless steel (SS) with Silconert coating that makes the surface inert. The disadvantage of this cylinder is that it is commercially available only in small volumes (3.6 L).

For formaldehyde, cylinder types B and D show the least adsorption.

For MT, the best performing cylinder is the Experis VOC type.

Interaction of methanol in dynamic conditions

In the second part of the research, the interaction of OVOCs with surface materials has been studied in a more fundamental way and in dynamic conditions.

Interaction of OVOCs with polymers like Polytetrafluoroethylene (PTFE) is in general very small and such polymer sampling lines are therefore widely used in the analysis of OVOCs. However, polymers have some characteristics which can cause undesirable effects like a relatively high permeability for gases (this can cause for example an offset in the measurements due to permeation of gases from the surroundings) or release of unwanted components (in particular when sampling lines need to be heated to avoid condensation). Stainless steel and other metal sampling lines are not gas permeable, yet many OVOCs strongly interact with such metal sampling lines. Measurement cells, pressure regulators, valves and flow controllers and many other parts are typically made of stainless steel. OVOC interaction with these parts can strongly impact their analysis.

Use of a passivation treatment can reduce the adsorption. Most notably Silcosteel (developed by Restek nearly 20 years ago) and its later derivatives have been shown effective in reducing adsorption for many (but not all) reactive gases. One of the newest passivation treatments is SilcoNert®2000 (proprietary coating technique of SilcoTek) which consists of a layer of amorphous silicon that is further functionalized and is applied via chemical vapor deposition.

Within this research project, the adsorption of methanol on sampling lines (polymer, metal and coated metal) was quantified using spectroscopic and gas chromatographic methods. The spectroscopic set-up developed at VSL is based on cavity ring down spectroscopy (CRDS) and it is shown in Figure 3. In panel A the mixture is first led through a bypass and then to the CRDS measurement cell. After switching two electronic valves,

the mixture is led via the test tube (panel B). The measured methanol concentration will temporarily decrease due to:

- Gas exchange (as the test tube was first filled with nitrogen)
- Adsorption of methanol in the test tube.

After making a correction for the gas exchange, the number of adsorbed molecules is determined from the measurement data. Data are then normalised to the inner surface area of the test tube in order to compare the adsorption of different materials under test.

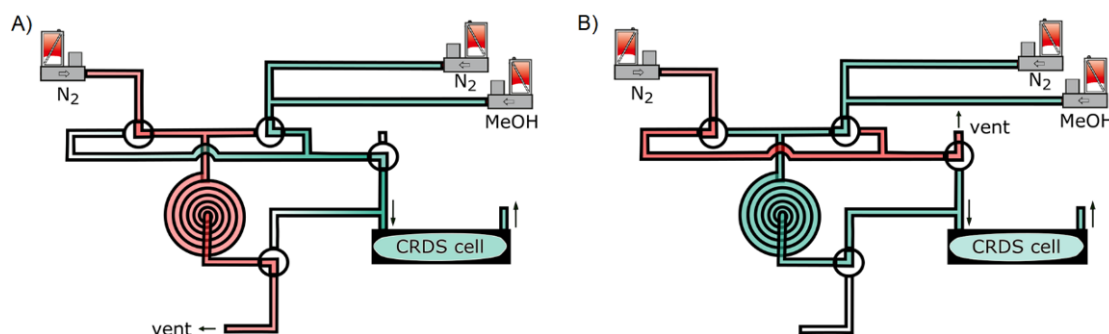


Figure 3: panel A) Initially a methanol mixture is sent to the CRDS measurement cell via a bypass while the test tubing is flushed with N₂. panel B) Methanol mixture is now sent through the test tubing and is then analysed by CRDS.

Figure 4 shows the results of the experiments for low concentrations of methanol at a flow of ca. 0.5 L/min passing through two identical uncoated (panel A) and coated (panel B) stainless steel tubing of 10 m length. For the uncoated tubing, it takes a long time (about 40 minutes) before the methanol reaches the measurement cell. After this, another 40 minutes are needed for the concentration to stabilize. For the coated tubing, the concentration stabilises in just around 1 minute. This indicates that the methanol adsorption in Silconert 2000 coated tube is much smaller than in the uncoated tube.

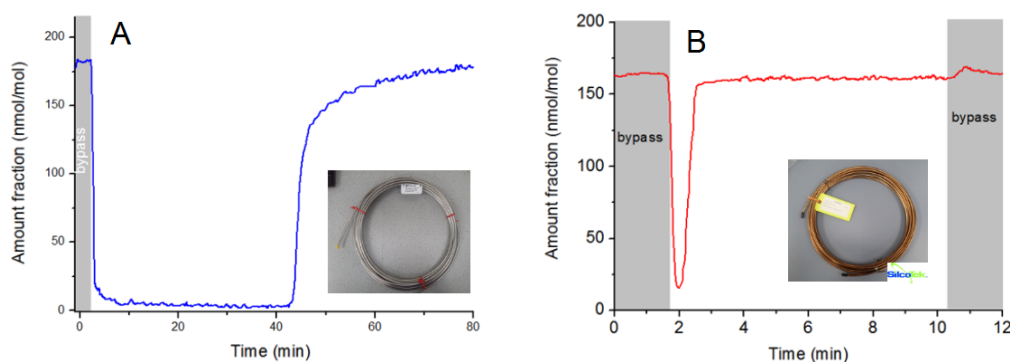


Figure 4 panel A: Result for an uncoated stainless steel tubing of 10 m length. Methanol mixture of 180 $\mu\text{mol/mol}$ is first led via a bypass (grey area) to the CRDS and then switched to the tubing. **Panel B:** Result for the same tube as in panel A but then coated with Silconert 2000. In this case only a very short dip is observed (of which about 30% is due to gas exchange).

From the experiments, it was observed that the least methanol adsorption is observed for polymer sampling lines, followed by coated metal sampling lines and highest adsorption was seen for uncoated metals. In field experiments sampling lines often need to be heated to avoid condensation. Therefore, experiments were also conducted at elevated temperatures (50 and 100 °C) by REG(DWD). The results of these experiments showed that many polymer sampling lines are not suitable for use at high temperatures as they start to emit compounds leading to spurious measurement signals. Coated sampling lines on the other hand are suitable for use at both elevated temperatures tested. Uncoated metals are not suitable.

Direct surface analysis of OVOC adsorption using X-ray spectroscopy

Within this project a novel measuring cell for in-situ metrology of VOC vapours and their sorption behaviour on different surfaces by means of X-ray absorption and reference-free X-ray fluorescence spectrometry was

developed by PTB. To use the unique possibilities of physically traceable (reference-free) X-ray fluorescence analysis (XRF) the cell was designed to allow for total-reflection XRF (TXRF) of a chosen substrate in a gaseous surrounding (gas cell) while the cell is compatible to PTB's instrumentation for X-ray spectrometry and can be operated at vacuum conditions to fulfil the XRF requirements for soft X-ray excitation and detection. This energy region is required to excite the main elements of carbon and oxygen in VOCs. PTB operates an undulator beamline for soft X-ray radiation at the synchrotron radiation facility BESSY II. By using radiometrically calibrated instrumentation and knowledge on the respective atomic fundamental parameters the mass deposition of an element detected can be traceably determined without any need of further calibration samples or reference materials. The developed gas-flow cell is shown in Figure 5.

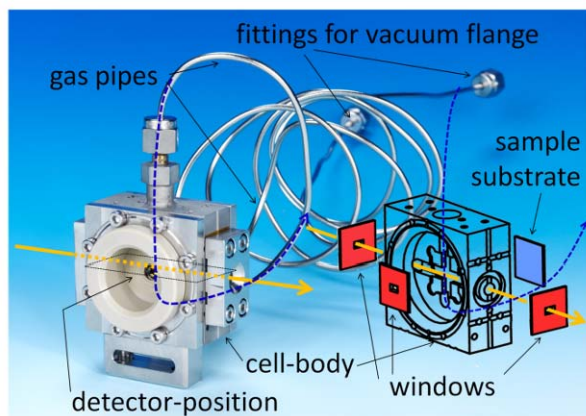


Figure 5: Photo and sketch of the gas-flow cell with labelling of the main components.

The photo shows the gas-flow cell with labelling of the main components. The sketch on the right-hand side depicts the gas-cell body and in an exploded view the three exchangeable Si_3N_4 -windows which can be placed at the body. In blue the location of the substrate of interest is shown. The yellow beam depicts the beam path for a transmission experiment through two of the windows allowing the measurement of the transmitted beam intensity. By slightly tilting ($< 3^\circ$) the gas-cell with respect to the incoming beam the sample surface is excited in total-reflection geometry which results in a high sensitivity for elements attached to the surface. Through the third window the element-specific X-ray fluorescence radiation can be collected by an energy-dispersive X-ray detector. This cell design allows for very small distances between the samples surface and the detector, thus again an optimal collection of the fluorescence photons from the surface. The application of such Si_3N_4 -windows with thicknesses down to 100 nm allows for the separation of the gas and the vacuum equipment.

The second methodology addressed with the novel gas-flow cell is the X-ray Absorption Spectrometry (XAS). XAS enables the analysis of (molecular) bonds and bond distances. By tuning the excitation energy over the absorption edge (binding energy of an inner shell electron) the shape of this absorption behaviour can be analysed. In general, the XAS structure differs for different species, thus allowing for the identification of chemical binding states. The gas-flow cell is designed for XAS experiments in transmission by a photodiode or by detecting the characteristic X-ray fluorescence line intensity of each excitation energy (fluorescence) by using an energy-dispersive detector. Both detection modes can be depicted in Figure 6.

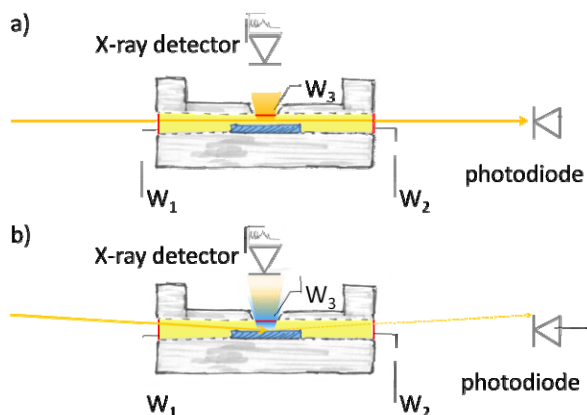


Figure 6: The sketches show both possible excitation geometries for the operation of the gas-flow cell. The three windows W1, W2, and W3 are depicted in red. The sample substrate for VOC sorption experiments in blue same as shown in fig.5 at the right side. a) transmission-mode, b) fluorescence-mode for TXRF analysis of the surface.

First experiments have been performed on Ethanol (EtOH) to test its adsorption on a metal surface (Figure 7).

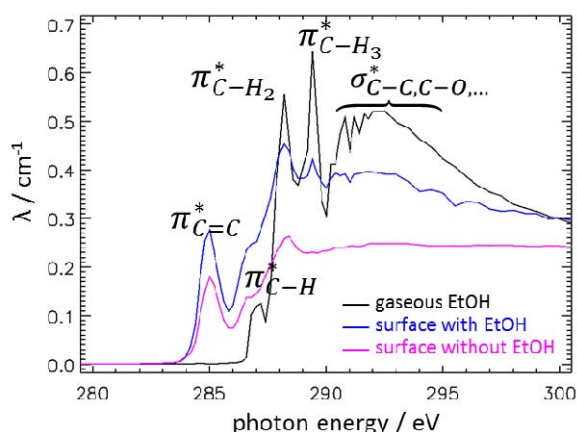


Figure 7: Experimental results to verify the adsorption of EtOH on a stainless steel surface.

The experiments were performed in the fluorescence-mode of the cell. For the sake of comparison, the black line shows the result from the EtOH in the gas phase measured in the transmission-mode. The blue line shows the calculated attenuation length from the XRF radiation coming from the sample surface in a 10 mbar EtOH (+ residual gas) atmosphere is shown. The pink line shows the surface signal from the stainless steel measured without EtOH in the gas-cell. The ordinate shows the determined linear attenuation coefficient λ of EtOH. The result corresponds to an EtOH pressure in the gas-cell of about 8 mbar which is in good agreement with the 10 mbar pressure measured at the gas inlet and 6 mbar at the gas outlet near the turbo pump. The initial experiments clearly indicated that it is possible to reveal information on the EtOH adsorbed at the surface. Further work will help to render this approach more quantitative by eliminating cross-contamination of the surface substrates employed by means of dedicated cap layers such as of Au. Hereby, PTB can offer full measurement capabilities for this kind of investigations.

3.1.2 Develop traceable standards for VOC-free zero gas and study the efficiency of purification technologies in removing VOC impurities at trace level concentrations (ppt)

For volatile organic compound (VOC) observations, zero gas is defined being hydrocarbon free like purified air or nitrogen and is essential for the characterisation of the measurement devices and procedures, for instrument operation as well as for calibrations. For that reason, different gas purifiers were tested for their removal efficiency of VOCs. A consistent measurements procedure was agreed by the testing labs of

REG(DWD), VSL and INRIM. Measurements were conducted with different gas chromatography (GC) instruments. See the set-up of the experiments in Figure 8.

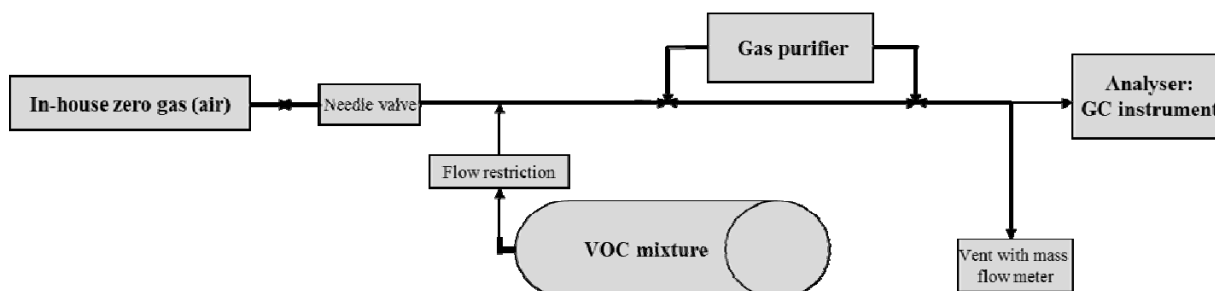


Figure 8: Experimental set-up for testing the purifier performance.

Two kinds of catalyst were tested, one with palladium and one with platinum. They were able to remove a large range of different VOCs (

Table 4). High mole fractions up to 50 nmol/mol were purified and residual concentrations were below the detection limits of the systems going down to less than 1 pmol/mol for Non-Methane Hydrocarbons (NMHCs). It was shown that it is important to conduct a cleaning procedure of the catalysts as they can emit some VOCs in early stages of use. Consequently, they were flushed with zero gas and held at operation temperature for at least two hours without connecting them to the measurement instruments.

Table 4: Tested VOCs by lab with the individual detection limits in pmol/mol.

	Compound	DWD	VSL	INRIM
NMHCs	Ethane	3	20	
	Ethene	7	21	
	Propane	2	10	
	Propene	3	11	
	Isobutane	1	10	
	Acetylene	10	15	
	n-butane	1	11	
	trans-2-butene	1	4	
	1-butene	2	4	
	Isobutene		6	
	cis-2-butene	1	3	
	Isopentane	1	3	
	n-pentane	1	8	
	1,3-butadiene	1	5	
	trans-2-pentene	1	13	
	1-pentene	1	3	
	2-methylpentane	1	6	
	n-hexane	1	1	
	Isoprene	2	4	
	n-heptane	1	4	
	Benzene	2	3	
	2-2-4-trimethylpentane	1	4	
	n-octane	1	5	
	Toluene	6	4	
	Ethylbenzene	5	7	
	p-, m-, o-xylene	5	6	
	1-3-5-trimethylbenzene	6	10	
	1-2-4-trimethylbenzene	2	16	
	1-2-3-trimethylbenzene	2		
Monoterpenes	alpha-pinene	4		
	myrcene	3		
	3-carene	2		
	cis-ocimene	2		
	p-cymene	2		

OVOCs	limonene	2		
	camphor	2		
	1,8-cineole	5		
	methanol	77	110	3
	acetaldehyde	84	110	
	ethanol	26	120	11
	acetone	31	80	11
Acetonitrile	MEK	2	180	
	methacrolein		110	
Acetonitrile		-	6	

A tested adsorption cartridge based on inorganic media was not suitable to remove light NMHCs (C_2 to C_4). There was a breakthrough behaviour of these compounds which was not constant. In Figure 9, the average output-to-input ratio for different input mole fractions and substances is shown. A ratio of 0% implies that the purifier removes the substance efficiently, whereas a ratio of 100% denotes a complete breakthrough of a substance. Also, VOC memory effects were observed. However, the adsorption cartridge removed heavier VOCs, OVOCs and monoterpenes. There was a high influence of humidity on the lifetime of this kind of purifier. The tested model in this study was only adequate for use with very dry air up to maximum 1 $\mu\text{mol/mol}$ water content. With this awareness, it is highly recommended to enquire the maximum applicable water content of the used gas from the manufacturer of a purifier.

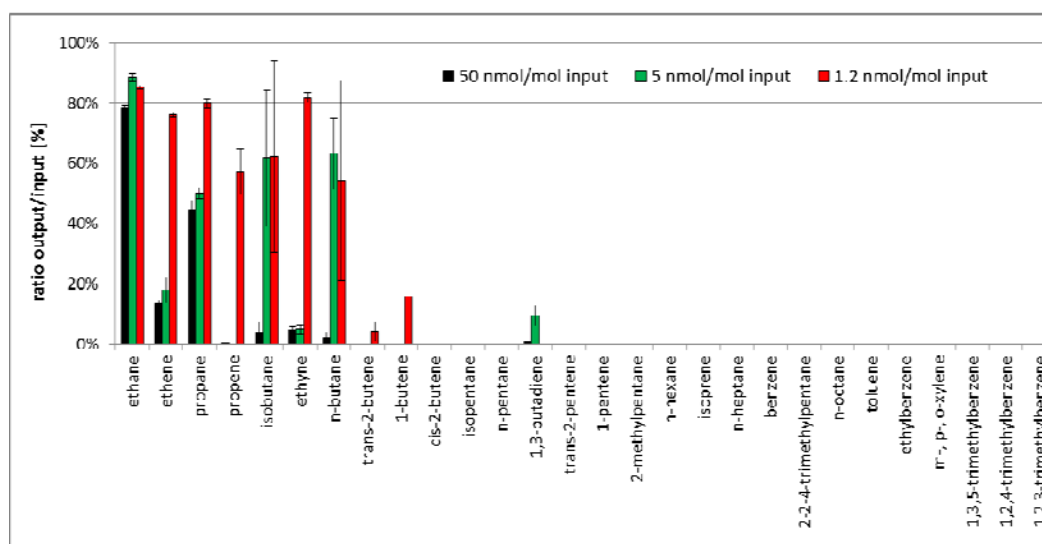


Figure 9: Results of the adsorption cartridge (ratios output/input) for an input of 50 nmol/mol (black), 5 nmol/mol (green) and 1.2 nmol/mol NMHCs (red). Error bars indicate the standard deviations of 5 measurements.

The details of the purifier testing are in publication stage in the journal “Atmospheric Measurement Techniques”. Title: “Preparation and analysis of zero gases for the measurement of trace VOCs in air monitoring” (Englert et al., REG(DWD) in collaboration with VSL, INRIM and REG(POLITO)).

3.1.3 Mathematical tools for calculating the uncertainty contribution of adsorption and reaction phenomena in sampling and dilution lines as well as for the gas treatment.

In addition to the experimental work on VOC adsorption on material surfaces, modelling studies have been performed by partner REG(POLITO) to better understand the experimental data and in some cases also to make predictions. The modelling studies focused on 2 cases:

- Calculating the uncertainty contribution of adsorption and reaction phenomena in sampling and dilution lines
- Calculating the uncertainty contribution of adsorption and reaction phenomena for the gas treatment

Some results of case a) are presented here.

Description of the model

During the measurement of oxygenated VOCs constant adsorption and desorption of molecules on the surface of the sampling system and analytical instrument take place. A simplified model was developed that estimates the adsorbed mass by means of a general first order equilibrium kinetic. The first order reaction was added to the transport equation in one dimension that considers a convective and a diffusive term. Computational Fluid Dynamics (CFD) was employed to estimate the back-mixing effect. Such effect was evaluated modelling the transport of the gas inside the experimental system to determine an effective diffusive coefficient without reaction. A source term was later added to the transport equation, which corresponds to the adsorption/desorption reaction.

The mass balance in the following equation introduces the term of “effective diffusion (D_{eff})” as a measure of the back mixing inside of the pipe. The adsorption rate is represented by the source term adsorption rate (R). The combination of CFD and numerical solving of the equation below allows the simulation of the adsorption phenomena that takes considerably less time than a full CFD simulation. The solution obtained from the model can be used to determine the value of the constant of adsorption K_{ads} , from a regression with experimental data.

$$\frac{dC}{dt} = -v \frac{\partial C}{\partial x} + D_{eff} \frac{\partial^2 C}{\partial x^2} - R$$

Considering the adsorbed mass as the product of a first order reaction, the rate of VOC loss is expressed as:

$$R = \frac{dC}{dt} = K_{ads}(C_{VOC} - C'_{VOC})$$

Where R , which is the rate of adsorption, depends on the concentration difference between the bulk and the wall, and a constant of adsorption K_{ads} . The uni-dimensional model considers that a single block of fluid moves at a certain velocity and does not interact with the adjacent fluid. The term of effective diffusion introduces the back mixing effect that takes place inside the real pipe. The CFD is used to determine the fluid dynamic effect without any wall interaction. Using the real geometry and conditions of the experiment, a CFD simulation is performed and the concentration at the outlet in time is obtained.

An initial value of the effective diffusion is used to generate a solution (without adsorption, $R = 0$). At this point a regression to minimize the sum of squares of the result and CFD is done, changing the parameter of effective diffusion until the error is minimized. Figure 10 represents the analysis involved in the estimation of both parameters.

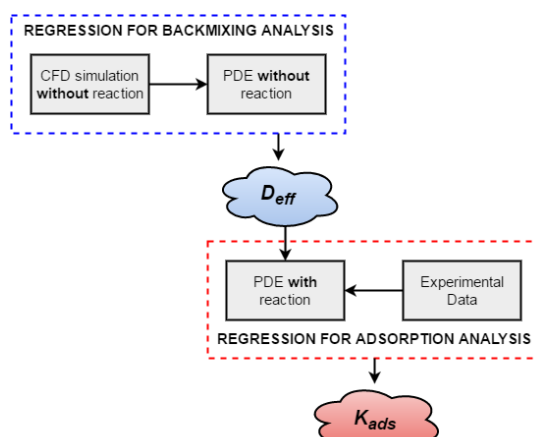


Figure 10: Simplified model for estimation of VOC-surface adsorption (PDE = partial differential equation).

After an effective diffusion is obtained, the simplified model is said to reproduce the fluid dynamic behaviour of the pipe, and at this point an estimation of K_{ads} is possible. A similar procedure to the estimation of the effective diffusion is done. Experimental data is directly compared to the results of the simplified model, changing the K_{ads} to minimize the sum of squares of the concentration at the outlet of the pipe.

Experimental versus modelling

Two experimental cases were simulated, in order to calculate the corresponding D_{eff} and K_{ads} . A regression was done over a set of experimental data generated by REG(DWD). A 3 $\mu\text{mol/mol}$ methanol in N_2 mixture was flushed at a flow rate of 15 SmL/min through a 10 m Sulfinert treated 304 stainless steel tube (0.216 mm internal diameter) kept at 50 °C. Replicating these conditions into the CFD model allows obtaining a response in time that can be used to determine the effective diffusion through regression. The algorithm minimizes the squared differences between both curves, and the best result against the experimental data is shown in Figure 11, panel A.

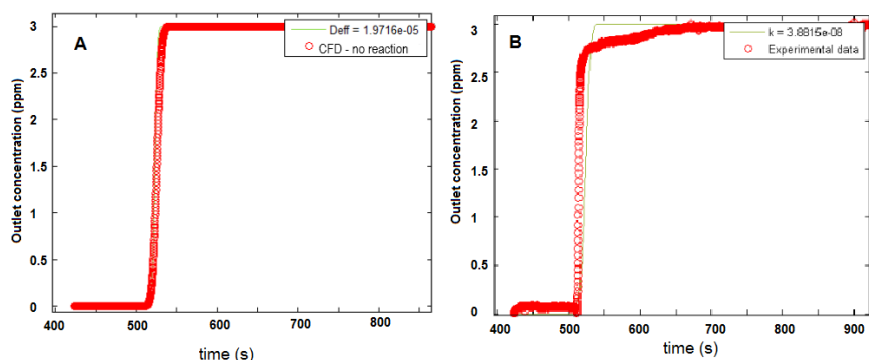


Figure 11: *panel A* CFD Simulation (no reaction) REG(DWD) system vs Simplified Model response. *panel B* Experimental data REG(DWD) vs Simplified model with reaction.

Including the effective diffusion from the previous regression, an iterative procedure that changes K to minimize the squared difference is done. At each step, a K is assumed, and the model is compared to the experimental curve. The best fit is shown in Figure 11, panel B. The residence time calculated with the reported flow rate for this case, did not match the residence time of experimental data. After correction for this, the time of saturation for the model is found to be 550 s against 650 s for the experimental data (i.e., around 15% difference).

Equilibrium prediction

In equilibrium the adsorbed mass is proportional to the molar concentration of the adsorbate through the equilibrium isotherm. An analysis of the equilibrium state predicted by the model was done, and Figure 12 shows the plot of the adsorbed VOC, q/A [$\mu\text{mol m}^{-2}$] as function of the concentration at the wall (relative to the bulk concentration).

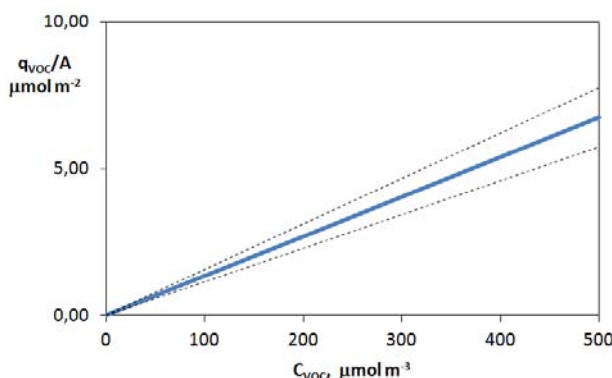


Figure 12: *Equilibrium Isotherm for acetone using Sulfinert treated tube material (only variability was considered for dotted lines)*

The simplest model of adsorption is given by Langmuir equation. This type of isotherm behaves differently at low or high concentration. The first part is characterised by a linear growth while at the second part, the equilibrium is not affected anymore by the concentration and the adsorbed mass remains constant as the total number of available sites is completely occupied.

Table 5 Kinetic constant (K_{kin}) and equilibrium constant (K_{eq}) for different tube materials and substances. Perfluoroalkoxy alkanes (PFA), Polyether ether ketone (PEEK), Sulfinert® (Restek proprietary coating)

↓Parameter	Material →	PFA	PEEK	Sulfinert	Sulfinert	Copper
VOC		Methanol	Methanol	Acetone	Methanol	Acetone
χ_{VOC} ($\mu\text{mol}_{VOC} \text{mol}^{-1}_{mix}$)		3	3	10	3	10
K_{eq} ($\text{m mol}_{VOC,ads} \text{mol}^{-1}_{VOC,mix}$)		$9.0 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$	$5.6 \cdot 10^{-2}$	1.0
$u(K_{eq})$ (variability only)		70%	64%	15%	32%	27%
Number of Data sets		1	1	6	1	7

Results of analysis on data sets from REG(DWD) and INRIM are summarized in

Table 5. The uncertainty of the constants was calculated accounting for variability of data only, with respect to stable zero gas responses, stable gas mixture responses and repetition of data sets.

Fluorinated polymers confirm the lowest affinity to methanol, but at this contact time permeation has low effects and aging of material could play a role. Copper confirmed a high affinity to VOCs and specifically to acetone. The variability of data can be reduced by both repetition of data sets and care on analysis procedures and devices.

3.2 Reference Standards to underpin atmospheric monitoring of VOCs

3.2.1 Develop traceable, accurate and long-term stable gaseous reference standards of key VOCs by static preparation method

Research is required to develop primary reference standards of reactive and short-lived compounds (e.g., oxygenated VOCs and monoterpenes) to underpin atmospheric monitoring of these key components. In order to satisfy the WMO GAW programmes data quality objectives, high accuracy standards with long term stability (> 2 years) are required at considerably lower amount fractions than are currently available (< 1 $\mu\text{mol/mol}$) with challenging low uncertainties (< 5 %) (Table 6). The availability of these standards is essential to ensure the accuracy and comparability of long-term VOC measurements needed for the evaluation of climate change and global trends in air quality.

Table 6: Target data quality objectives for developing gas standards for atmospheric monitoring

Testing NMIs	Class of components	Composition nmol/mol	Uncertainty %	Stability years
VSL, NPL, CMI	Oxygenated VOCs (OVOCs)	100 1000 (CMI)	5	2
NPL	Monoterpenes (MT)	2	5	2
NPL, LNE	Formaldehyde (F)	1000	5	2

High accuracy static reference standards of OVOCs (NPL, VSL), formaldehyde (NPL, LNE) and monoterpenes (NPL) were prepared at 100 nmol/mol, 1000 nmol/mol and at 2 nmol/mol, respectively, in nitrogen in cylinders with different passivation treatments using both those that are currently available and employed at NMIs and new and promising ones provided by gas specialty producers. CMI also prepared ethanol binaries and ethanol ternary mixtures at 1000 nmol/mol. As described earlier in 3.1.1, the cylinder treatments were evaluated with decanting experiments to determine the most appropriate for the different compounds and the results were used to determine which to use for the long-term stability trials.

In consultation with the WMO GAW VOC network, a priority list of OVOCs and monoterpenes was produced, at the beginning of the project, identifying the key compounds that would have the greatest impact on the atmospheric monitoring community if standards were developed for them. Using this and the results of the decanting experiments, NPL prepared methanol, ethanol, acetone and n-hexane standards in nitrogen at

nominally 100 nmol/mol in Spectraseal treated cylinders (BOC /Linde proprietary treatment technique) and type B cylinders. The n-hexane was included as an internal standard. VSL prepared methanol, ethanol, acetone, methyl ethyl ketone (MEK), methyl vinyl ketone (MVK), methacrolein, acetaldehyde, propane and n-hexane in nitrogen at nominally 100 nmol/mol in type A, B, C, D cylinders and Silconert 2000 coated stainless steel cylinders purchased from Swagelok. NPL prepared α -pinene, Δ^3 -carene, limonene, 1,8-cineole and octane standards in nitrogen at nominally 2 nmol/mol in Air Products cylinders with Experis proprietary treatment. NPL and LNE prepared formaldehyde in nitrogen at nominally 1 μ mol/mol in type B, D (NPL) and type A, B, D (LNE) cylinders. In addition, LNE also used two other cylinder treatments commonly used at their laboratories for other gas mixtures (designated here as type E and F). All these mixtures were studied over a 12 – 24 months period to determine long term stability.

The results from NPL and LNE show that it's very difficult to identify cylinders which lead to formaldehyde gas mixtures at 1 μ mol/mol with amount fractions stable over the time. This study shows that the most suitable types of cylinder are the type A and F with respectively an amount fraction decrease of -5.6 % to -7.3 % and -3.5 % to -5.0 % over a time period of 15 months.

The results from NPL show that the Air Products Experis are the most appropriate cylinders for preparation of low amount fraction monoterpene standards. Over the course of 1 year all 4 components appear stable. However, changes to the analytical column and the instrumentation used during the stability measurements significantly complicated the analysis and should be discouraged.

The results of the study conducted by NPL showed that both type B and BOC Spectraseal cylinders appear to be appropriate for methanol, ethanol and acetone. However, the results of the comparison carried out in this project demonstrated that, due to surface adsorption, methanol and ethanol (less significant) results in amount fractions in cylinders are not representative of the gravimetric value and a correction is required.

The results of the study from VSL show that Silconert-2000 coated stainless steel cylinders are the most suitable cylinder type for the preparation of OVOCs gas standards at 100 nmol/mol in nitrogen, showing the least interaction with OVOCs (insignificant adsorption effect) and the best stability over a period of 19 months. According to the same study, also type B cylinder, with exception of methanol, is suitable for the preparation of OVOCs gas mixtures at 100 nmol/mol (for methanol and ethanol corrections of the gravimetric values have been applied using in-house dynamic gas standards). Further study will be necessary to confirm longer term stability.

In conclusion, acetone, MEK, MVK, methacrolein static gas standards at low amount fractions (100 nmol/mol) are complying with the target DQOs of 5 % expanded uncertainty. Methanol and ethanol standards cannot rely on the gravimetric preparation in aluminium cylinders as this is clearly not representative of the concentration of the prepared mixtures due to the adsorptive losses to the cylinder walls and valve. For stainless steel Silconert coated cylinders, the adsorption losses of these gases are not significant. However, because these standards were obtained by dilution of concentrated standards in aluminium cylinders, also these standards were affected by losses of methanol and ethanol. Acetaldehyde gas standards show inconsistent and puzzled trends on the analysed amounts of fractions over both short-term and long-term periods, further investigation is required to be able to draw clear conclusions.

3.2.2 Develop traceable and accurate gaseous reference standards of key VOCs by dynamic generation methods

Two partners, namely METAS and INRIM, designed and built two transfer gas standards, namely two portable VOC gas generators, able to produce low ppb levels of VOC making use of dynamic generation methods (Figure 13).

INRIM designed and constructed a novel mobile gas generator for oxygenated-VOCs mixtures at trace levels. The vapours of three components: methanol, ethanol and acetone, were simultaneously generated and mixed with a controlled stream of zero air to obtain target amount fractions of 100 nmol/mol. The vapour generation is based on diffusion (ISO 6145-8 method).



Figure 13: Photos of the two portable generators for VOCs built by METAS (left) and INRIM (right).

METAS designed and built a new transportable gas generator (ReGaS2 – Reactive Gas Standard 2) producing SI-traceable reference gas mixtures up to 5 VOCs simultaneously. The generation method is based on permeation and further dynamic dilution. The stability and reproducibility of the gas mixture produced with ReGaS2 was tested for two compounds and was better than 1.5% (

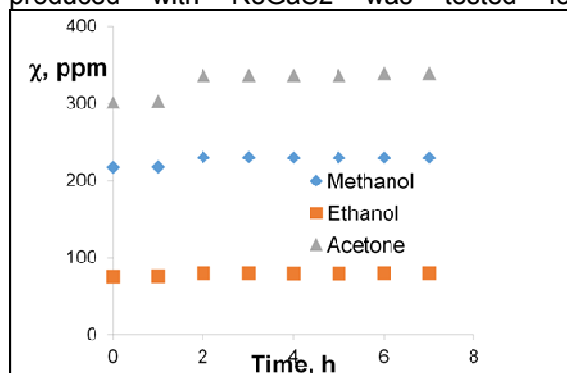


Figure 14 left). During the project, reference gas mixtures of limonene, ethanol and methyl vinyl ketone (MVK) were produced and compared with other institutes. The uncertainty of the reference gas mixtures – about 7% ($k=2$) - is highly dominated by the reproducibility of the permeation rate of the permeation unit itself which was between 3 and 6 % for the VOCs tested in this project. This could be improved by changing the working conditions (e.g. using higher temperature) and/or the permeation device properties.

INRIM designed and realized a transportable generator, based on diffusion, to produce mixtures at ppb level of oxygenated compounds. The mixtures are SI-traceable, the generator works currently with up to 4 VOCs with stability and reproducibility that was tested better than 1% on 6 months. Time to stability after a restart was determined around 6 hours (Figure 14: **(Left) Stability and reproducibility test for ReGaS2 generating about 100 ppb (mol/mol) of MVK. Analysis with ATD-GC-FID**right). During the project methanol, ethanol and acetone gas mixtures were produced and compared with other institutes. The portability of the device was problematic because of issues with the thermal control system. The data generated by this device were evaluated by REG(POLITO)

A joint article on the performance of the two portable generators has been recently published in Analytical and Bioanalytical Chemistry, “Compact devices for generation of reference trace VOC mixtures: a new concept in assuring quality at chemical and biochemical labs” (M. Lecuna et al.).

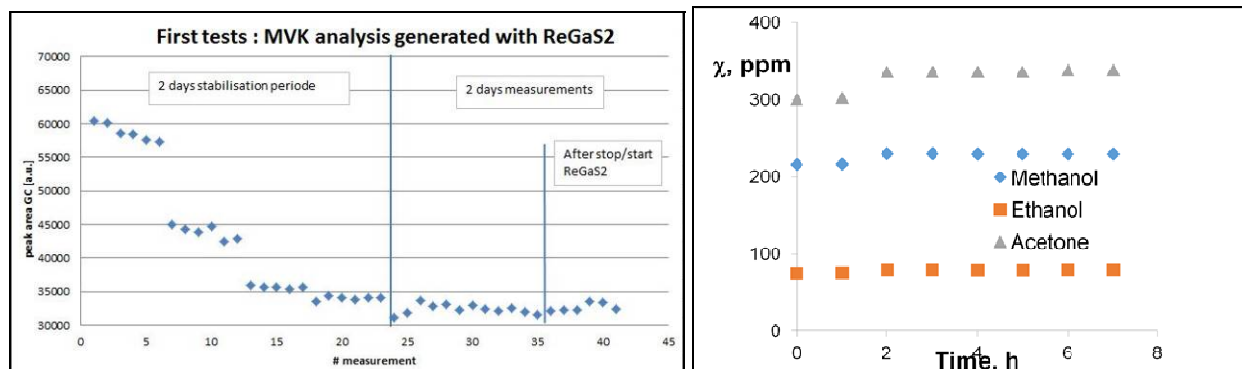


Figure 14: (Left) Stability and reproducibility test for ReGaS2 generating about 100 ppb (mol/mol) of MVK. Analysis with ATD-GC-FID. (right) Stabilization period of INRIM portable device after restart

3.2.3 Validate the VOC gas standards developed to underpin atmospheric monitoring by organisation of a comparison among the project partners

During this comparison, NPL and VSL exchanged their standards in cylinders containing OVOCs at nominally 100 nmol/mol (NPL: methanol, ethanol and acetone; VSL: methanol, ethanol, acetone, methyl ethyl ketone, methyl vinyl ketone, methacrolein and acetaldehyde). VSL sent also a 7 component OVOC standard to REG(DWD), IMT Lille Douai and other members of the ACTRIS project and this round robin is continuing beyond the life of the project. METAS sent the ReGaS2 for a 4-5 months period to VSL and to NPL to measure the reference gas mixtures of ethanol, methyl vinyl ketone and limonene produced dynamically by the portable generator and compare them with the NPL and VSL developed standards. In the same way and in the same period, INRIM portable generator for methanol, ethanol and acetone gas mixtures, was measured by NPL and VSL. LNE sent a gas standard of formaldehyde at 1 $\mu\text{mol/mol}$ to NPL and TUBITAK.

The results of the comparison show that:

- There was very good agreement between VSL cylinders, VSL dynamic preparation by diffusion (methanol, ethanol and acetone) and the METAS permeation device (ethanol).
- The positive bias observed for NPL compared to VSL and METAS is likely due to adsorptive losses of methanol and ethanol to the cylinder walls that are currently not corrected for. NPL is actively working on developing alternative dynamic preparation approaches to resolve this. The very good agreement, within uncertainties) between NPL and VSL for acetone indicates that adsorption to the cylinder walls and valve even at 100 nmol/mol is minimal and shows that the gravimetric valve is representative of the amount fraction of these acetone mixtures.
- The poor comparability to the static NPL and VSL reference standards and to the METAS device and the inconsistency in the results for the INRIM device between operation at NPL and VSL suggest that the INRIM device was operating differently at VSL and NPL, which may have affected the generated values. Further work is required here to achieve a better thermal control of this device before it is ready for use in field calibration.
- The differences between the gravimetric values provided by CMI and the assigned analytical values from NPL suggests that the uncertainty assigned by CMI is likely underestimated and that cylinder to cylinder variability in preparation could dominate the uncertainty although this has not been included. However, the results suggest that CMI have improved their preparation capabilities during the course of the KEY-VOCs project, which is encouraging.
- The preliminary results of the comparison with the ACTRIS laboratories, show that there is good agreement, within uncertainties, VSL cylinder (7 OVOCs) and standards used at REG(DWD) and IMT Lille Douai.
- The good agreement, within uncertainties, for formaldehyde between NPL, LNE and TUBITAK is also good considering the challenging nature of this compound.

- The comparison of limonene generated dynamically by the METAS permeation device and the static reference standards produced by NPL shows a discrepancy of 0.8 nmol/mol for a nominal 4 nmol/mol mixture (25%). This discrepancy suggests either a systematic bias between the two approaches or an underestimation of uncertainty by either METAS, NPL or both. A systematic bias seems more likely given the NPL's recent performance in a CCQM (Consultative Committee for Amount of Substance) comparison (K121 – Terpenes in air) with NIST and KRISS and the calculated uncertainty for the METAS device for ethanol and MVK being in line with the static mixture from VSL. Sources of systematic bias are currently being investigated but purity analysis may play a role in the determination of a larger than actual permeation rate for limonene.

3.3 Development of Gas Standards to underpin Indoor Air measurements

3.3.1 Development of reference gas standards for key polar-VOCs for indoor air QA/QC activities.

The preparation of reference materials containing polar organic compounds (p-VOCs), realised by INRIM, follows ISO 6145-8 "Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 8: Diffusion method". Mass fractions of VOC at trace level in air are prepared by diffusion of the calibration VOCs through diffusion tubes, in a carrier gas flow. The diffusion vial consists of a reservoir containing the liquid VOC and a neck through which evaporated molecules are migrating (Figure 15). A special diffusion cell is realized to allow flushing the vial top with a thermal conditioned laminar flow of the carrier gas, producing a continuous flow from the diffusion cell.

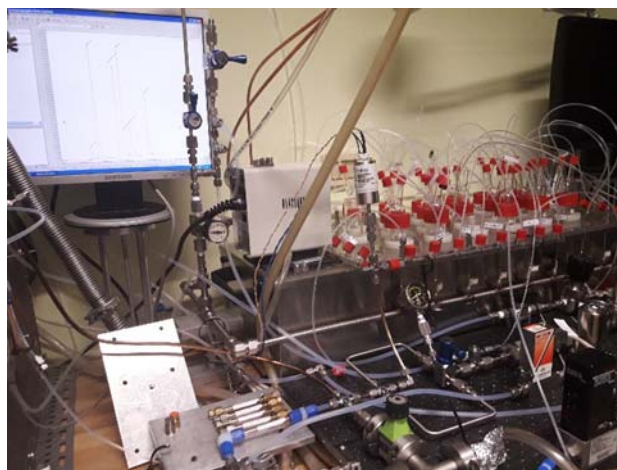
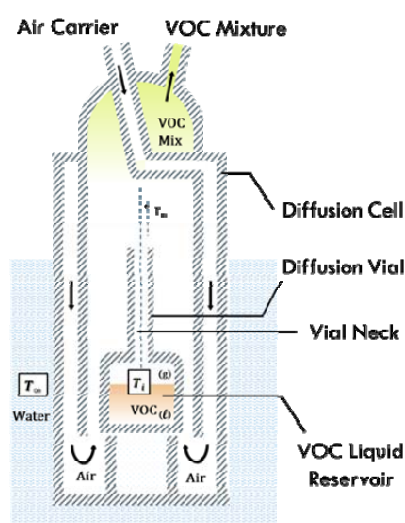


Figure 15: The INRIM dynamic generator of p-VOC mixtures

The mass fraction produced by the diffusion cells is further diluted with a single stage air dilution flow in order to reach the required mass fractions at trace level. A purified air flow rate of 10-25 L/min at standard conditions (273.15 K and 101325 Pa) is mixed in the dilution line with the VOC diffusion rate D_R in the range 0.1-10 $\mu\text{g}/\text{min}$ coming from the generation line, carried up by purified air flow rate in the diffusion cells of around 50 mL/min at standard conditions. A portion of the prepared mixture in the dilution line is sampled in a sampling line for gas chromatographic (GC) measurement. A pure air flow is also sampled in the GC for zero air purity measurement.

The preparation of transfer standards as certified reference materials proceeds via pumped sampling of known volumes of the p-VOC dynamic gas mixture into thermal desorption tubes (TD tubes) according to ISO 16017-1 "Pumped sampling".

Table 7: p-VOCs and sorbent materials used for the storage test

p-VOC	Sorbent material
Hexanal	Tenax TA
n-Butanol	Tenax TA – Carbograph 1TD
Cyclopentanone	(loaded amount ~200 ng/component/tube)
2-Isopropoxyethanol	
Acetic acid	

When preparing transfer standards, a known volume of a dynamic gas mixture is sampled for a known time into TD-tubes containing a known mass of a known sorbent. A storage test was performed to determine the stability of p-VOC transfer standards and the most suitable sorbent material for p-VOCs. Therefore, five different p-VOCs were loaded onto two different sorbent materials (Table 7).

After preparation, the transfer standards were stored at -20 °C and +20 °C and analysed by TUBITAK according to the scheme given in Table 8.

Table 8: Overview stability program for p-VOCs

	1 day	14 days	3 months	6 months	Description
-20 °C	X		X	X	Freezer and transport
20 °C		X	X	X	Standard and transport

Tenax TA and Tenax TA - Carbograph 1TD gave similar results for all the p-VOCs. Generally, after two weeks, the compounds were not stable at +20 °C on both types of sorbent tubes. Here, hexanal, n-butanol and acetic acid were most unstable. Sorbent tubes kept at -20 °C gave better results. When cooled, the standards were stable for up to three months.

The uncertainty of dynamic p-VOCs gas mixtures was evaluated by REG(POLITO). Some uncertainty sources result in uncertainties are negligible, namely: leakage mass flow rate, VOC-wall interaction flow rate, gas mixing, experimental mass fraction repeatability. Main contributors to the uncertainty of the diffusion coefficient (D_R) are:

- $u(m)$: mass [g]
- $u(\phi_1)$: main dilution flow rate

For the preparation of the transfer standards the uncertainty budgets of VOC breakthrough, diffusion on closed tube and flushing on open tube are negligible. Main contributors here are:

- $u(c_{VOC})$: mass fraction [ng/g]
- $u(\phi_s)$: sampling flow rate [g/min]
- $u(t_s)$: sampling time [min]

The grouped uncertainties for the different p-VOCs in transfer standards are displayed in Table 9 for a loading amount of 200 ng of component in the TD-tube.

Table 9: Loaded mass uncertainties ($k=2$) for p-VOC

p-VOC	$u(D_{R_gen})$
Hexanal	5%
1-Butanol	4%
Cyclopentanone	4%
2-Isopropoxyethanol	4%
Acetic acid	5%

3.3.2 Development of reference gas standards for key S-VOCs for indoor air QA/QC activities.

For the preparation of reference materials containing semi-volatile organic compounds (S-VOCs) VSL has a unique dynamic gas mixture preparation system, working according to ISO 6145-4 "Continuous syringe injection method". S-VOCs have boiling points between 240 and 400 °C and low vapour pressures. To obtain traceable and accurate dynamic gas mixtures containing S-VOCs a set-up is built inside an oven (fig.Figure 16).

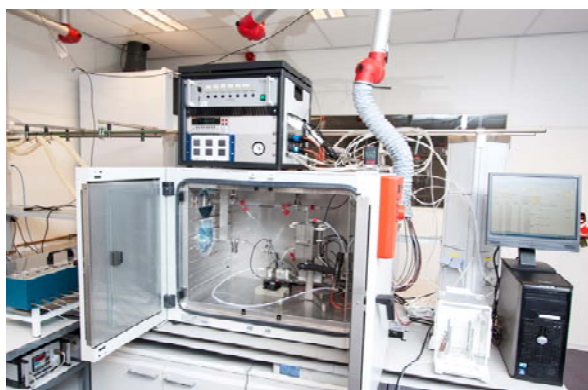


Figure 16: Picture of the dynamic gas mixture preparation set up in the laboratory of VSL in Delft, the Netherlands.

The temperature in the oven is kept at 80 °C to prevent condensation of the S-VOCs in the gas mixture. A known liquid mixture of S-VOCs is prepared by gravimetry and is diluted in a known amount of methanol. This liquid mixture is forced through a capillary with a controlled flow stream. This solution flows into a small oven where it evaporates at 150 °C. Subsequently the vapours are diluted with a known flow of zero gas. A dynamic S-VOC gas mixture is created. The gas mixture is traceable to the kilogram and m³/s:

- Kilogram: A calibrated analytical balance is used to prepare the S-VOC solution and to weigh its mass flow through the capillary at regular intervals.
- m³/s: Primary flow piston provers are used to calibrate the zero gas dilution flow.

Transfer standards were prepared as explained in 3.3.1a. A storage test was performed to determine the stability of S-VOC transfer standards and the most suitable sorbent material for S-VOCs. Therefore, eight different S-VOCs were loaded onto four different sorbent materials (Table 10).

Table 10: S-VOC and sorbent materials used for the storage test

S-VOC	Sorbent material
Decane (n-C10) (Reference)	Tenax TA (TTA)
Hexadecane (n-C16)	TTA CG1
Naphthalene	TTA CG5
Dodecamethylcyclhexasiloxane (D6)	TTA coated
Butylated hydroxytoluene (BHT)	(loaded amount ~50 ng/per component/tube)
Octadecane (n-C18)	
Dibutyl phthalate (DBP)	
Eicosane (n-C20)	

After preparation, the transfer standards were stored at -20 °C, 20 °C and at +40 °C and analysed according the scheme given in Table 11.

Table 11. Overview stability program for S-VOCs

	1 day	14 days	1 month	3 months	6 months	Description
-20 °C			X	X	X	Freezer
20 °C	X	X	X	X	X	Standard

+40 °C		X				Transport
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After analysis of all the transfer standards by TD-GC-FID, it seems that the coated TTA sorbent material is the best choice for all the S-VOCs. Storage at 40 °C for two weeks does not influence the stability of the S-VOCs except for BHT, this compound degrades when stored at 40 °C. Storage of the transfer standards at -20 °C improves the stability of BHT up to one month instead of two weeks at room temperature. All the S-VOCs can be stored for 6 months at 20 °C on the TTA coated sorbent material except for BHT, which is only stable up to 1 month at -20 °C.

In order to calculate the uncertainty of dynamic S-VOCs gas mixtures obtained with the set-up in Figure 16, different uncertainty sources were evaluated. Some of these sources result in uncertainties which are negligible compared to other uncertainty contributions, namely: buoyancy, time and purity of zero air and nitrogen. The uncertainty sources that do result in a significant contribution are:

- U_{grav} (weighing): ≤ 0.5 %
- U_{flow} (dilution flow): 0.6 %
- U_{pur} (purity of the S-VOCs)
- U_{mis} (miscibility)
- U_{cond} (condensation)

The grouped uncertainties for the different S-VOCs in the dynamic gas mixture are displayed in Table 12. These figures have been calculated for dynamic gas mixtures containing 40 $\mu\text{g}/\text{m}^3$ of the different S-VOCs.

Table 12: Expanded uncertainty of dynamic gas mixtures containing S-VOCs prepared via continuous injection ($k = 2$) and of transfer standard tubes charged with the dynamic gas mixture

Component	Dynamic S-VOC gas mixture at 40 $\mu\text{g}/\text{m}^3$ U_{con} (% , $k=2$)	Transfer standard tube containing 50 ng S-VOCs U_{con} (% , $k=2$)
Decane (n-C ₁₀)	2	2
Naphthalene	3	3
Dodecamethylcyclotetrasiloxane (D6)	3	3
Hexadecane (n-C ₁₆)	5	5
Butylated hydroxytoluene (BHT)	5	5
Dibutyl phthalate (DBP)	10	10
Octadecane (n-C ₁₈)	7	7
Eicosane (n-C ₂₀)	7	7

In the same table, the expanded uncertainties relative to the preparation of S-VOC in transfer standard tubes are shown. The uncertainty sources for time, loading efficiency and desorption efficiency are negligible compared to:

- U_{conc} (concentration)
- U_{flow} (dilution flow)

These figures have been calculated for transfer standards containing 50 ng/tube of the different S-VOCs. As it can be seen, the uncertainty due to the charging of the tubes with pumped sampling of a known mass of S-VOCs does not change the final uncertainty with respect to that of the dynamic gas standards.

3.3.3 Develop reproducibly emitting polymer materials for the quality control of emissions testing procedures (e.g. emission test chamber method).

A synthetic material that reproducibly emits VOCs was developed at BAM. As test compounds 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (Texanol®, CAS 25265-77-4), styrene (CAS 100-42-5) and 2,6-diisopropyl-naphthalene (DIPN, CAS 38640-62-9) were chosen. Texanol® is a VOC in the border area to the

S-VOCs and a typical emittant from latex paints. Styrene is a typical VOC of relatively high volatility and DIPN is an S-VOC typically emitted from recycled paper.

It is necessary to have a material that behaves like a typical specimen investigated in emission test chambers (e.g. building materials, furniture), which should be used for quality control and assurance (QA/QC) of the emission test chamber method. The use of such materials is recommended by the test standard EN 16516: 2017. It is also important that the emitting compounds cover a broad range of volatility. However, this special reference material has the problem that it must release VOC during its usage, which is connected to a reduction of the complete amount enclosed in the material. For chamber tests this material must be stored very tightly before starting the test. Another requirement is that the decay curve of the emitting VOCs must be reproducible over a minimum period of one week. These tests should be carried out under dynamic conditions with a defined air exchange rate inside of the chambers.

After intensive testing, thermoplastic polyurethane (TPU) was selected as suitable carrier matrix (Figure 17). The TPU pieces were impregnated with the selected compounds in a high-pressure cell with liquid CO₂ as solvent. The CO₂ enables substances to pass amorphous and semi-crystalline polymeric matrices as the polymer chains get movable, so CO₂ as well as the VOC can diffuse. After the pressure holding time the chamber was depressurised slowly. The CO₂ leaves the polymer, thus, the VOC remains in the polymer matrix. As suitable impregnation parameters were found: temperature: 20 °C, pressure: 280 bar, S-VOCs injection volume: 6 mL, pressure holding time: 20 min.

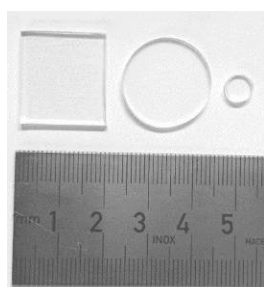


Figure 17: Surface sizes of the investigated TPU samples (left: 9.6 cm², middle: 7.5 cm², right: 0.94 cm²).

Figure 18 shows the area specific emission rates (SER_a) over time for three pairs of independently TPU samples impregnated with texanol. It is noticeable that the SER_a of samples 16 a+b decrease faster than the ones of the other four samples. However, in all cases the emission profiles of the TPU plates impregnated in parallel (a+b) run similarly. Therefore, it is useful to impregnate all samples together in one batch. Furthermore, the use of the material immediately after production is not useful due to the high variances of the SER_a in the first days. It is rather indicated to age it, since it could be observed that the deviations between the emission profiles of samples 17 (a+b) and 18 (a+b) became smaller between the 7th and 14th day after chamber loading.

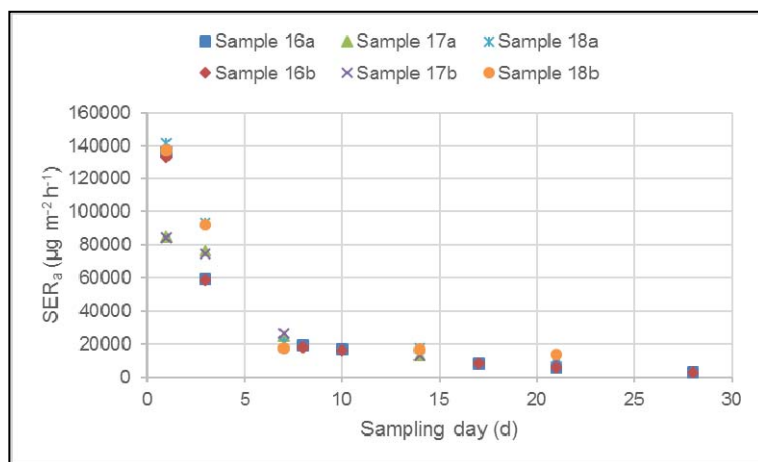


Figure 18: SER_a over time of samples 16a+b, 17a+b and 18a+b impregnated with texanol in three independent batches.

After sample preparation, the impregnated TPU pieces were sealed with aluminium-coated polyethylene foil (Al/PE). For testing the long-term stability, the sealed samples were stored for different times (6 and 48 days) in the refrigerator at 7 °C. They were unsealed only shortly before loading into the test chamber. The test revealed a similar course of SER_a as depicted in Figure 18, also with differences in the first days followed by convergence after ca. 10 days, indicating again the necessity of material aging prior to use in emission test chambers.

In another experiment, it was tried to transfer the impregnation conditions from texanol to styrene, DIPN and a combination of both. As a result, it became obvious that the impregnation conditions of texanol to the volatile compound styrene could be well transferred, as reproducibility in TPU preparation was shown, different to DIPN, which could not be exhaustively explained.

Summarized, the objective of this study could successfully be realised: a material, which fulfils requirements such as a homogenous and reproducible release of VOC as well as long-term stability of at least seven weeks, was developed and intensively tested for texanol, chosen as a VOC with a comparatively low volatility. However, some of the results can be regarded as indicative, so there are still some aspects which require further investigation, e.g. transfer of the impregnation conditions to other VOCs and impregnation with solid compounds like 2,6-diisopropylnaphthalene (DIPN). It could be shown that the reproducibility of TPU samples impregnated with the two VOCs texanol and styrene was good, whereas it was not for the SVOC DIPN. In order to handle the different physicochemical properties, it will be necessary to adjust the impregnation conditions for each compound of interest. It might be easier to impregnate several individual TPU samples to generate a VOC mixture in emission test chambers than to impregnate one TPU sample with several VOCs.

The details and results of this work is published in two articles: “Reproducibly emitting reference material on thermoplastic polyurethane basis for quality assurance/quality control of emission test chamber measurements”, M. Richter et al, in Building and Environment (Reference 2) and “Reproducibly emitting reference material for volatile and semi-volatile organic compounds – using finite element modelling for emission predictions“, B. Mull et al. in Air Quality, Atmosphere & Health.

3.3.4 Validate the VOC gas standards developed to underpin indoor air quality by organisation of a comparison among the project partners.

For the validation of the p-VOC and S-VOC gas standards developed to underpin indoor air quality and more specifically emission testing, Tenax TA sorbent tubes were loaded with both component groups. Three NMIs (in random order BAM, TUBITAK and VSL) and two Collaborators took part in the comparison. One collaborator withdrew from the comparison later (*Table 12: Expanded uncertainty of dynamic gas mixtures containing S-VOCs prepared via continuous injection ($k = 2$) and of transfer standard tubes charged with the dynamic gas mixture* Table 12).

The participants' capabilities in measuring S-VOCs and p-VOCs in Tenax TA sorbent tubes were being demonstrated through this comparison. For S-VOCs most of the participants successfully measured C10, D6, BHT, C16, C18, DPB and C20 in most of the sorbent tubes. In general, results show consistency with the reference value within the associated uncertainty. All the participants except NMI-1 and the collaborator show inconsistent results for most of the sorbent tubes loaded with naphthalene. For p-VOCs, participants show inconsistent results for most of the sorbent tubes loaded with butanol, hexanal, acetic acid and cyclopentanone. For isopropoxyethanol, most of the results agree to less than 20% relative deviation of the reference value and is consistent with the reference value within the associated uncertainty.

Table 13: Results of S-VOC and p-VOC measurements (RV – reference value)

Name of VOCs	NMI-1	NMI-2	NMI-3	Collaborator
n-C10 (RV = 52 ng)	50.5±1.2ng to 52±1.2ng	52±1.1ng to 57±1.2ng	-	-
Naphthalene (RV = 51 ng)	49.1±1.1ng to 50.5±1.2ng	49±1.8ng to 61±2.3ng	54.4±2.9 to 57.6±3.1	46.1±7.4ng to 49±7.8ng
D6 (RV = 52 ng)	50.5±1.4ng to 52.0±1.4ng	47±1.0ng to 55±1.2ng	48.5±2.4ng to 54.4±2.7ng	-
BHT (RV = 52 ng)	48.7±2.6ng to 51.3±1.6ng	41±1.3ng to 58±1.9ng	47.1±3.6 to 51±3.9ng	-
n-C16 (RV = 56 ng)	52.9±1.2 to 56.9±1.3ng	47±1.1ng to 59±1.4ng	-	-
n-C18 (RV = 51 ng)	48.6±1.3ng to 51.9±2.2ng	45±0.9ng to 52±1.0ng	51.8±3.2ng to 53.5±3.3ng	-
DBP (RV = 44 ng)	40±1ng to 44±5ng	40±1.3ng to 46±1.5ng	40.5±2.0ng to 45.6±2.3ng	-
n-C20 (RV = 48 ng)	44±1ng to 50±5ng	44±1ng to 53±1.2ng	45.3±2.2ng to 54±2.7ng	-
Butanol (RV = 313 ng)	-	349±10.4ng to 391±11.7ng	310.7±9.8ng to 356.1±11.3ng	-
Hexanal (RV = 270 ng)	-	153±24.1ng to 205±32.2ng	276.3±7.6ng to 315.0±8.7ng	-
Acetic acid (RV = 449 ng)	-	546±72.5 to 913±121.1ng	387.9±13.4ng to 515.3±17.8ng	-
Cyclopentanone (RV = 258)	-	339±24.9ng to 364±26.7ng	249.5±8.6 to 292.2±10.0	-
2-Isopropoxy ethanol (RV = 190 ng)	-	192±7.6ng to 221±8.7ng	174.3±5.3ng to 210.3±6.4ng	-

3.4 Validation of measurement systems (sensors and portable devices) commercially available for the measurement of VOCs

While the current sensor technology can be considered efficient enough for inorganic gases such as CO, CO₂ and to a lesser extent O₃ and NO₂¹, this is not the case for volatile organic compounds (VOCs) and in particular BTEX (Benzene, Toluene, Ethylbenzene and Xylene). In the most recent review of sensors for the measurements of VOCs in ambient air², the authors concluded that the current sensor technology is not yet able to measure the concentrations expected in ambient air and that they generally suffer from poor selectivity.

The Air Quality Directive of the European Union (2008/50/EC) defines as mandatory the monitoring of benzene in ambient air. In particular, it allows the use of indicative measurement methods but it requires the use of a selected method to meet a defined Data Quality Objective (DQO) of 30%. This DQO is defined as the relative expanded uncertainty of measurement and it shall be assessed in the region of the limit value (LV) of about 1.5 ppb for the annual mean.

¹ Spinelle, L.; Gerboles, M.; Alexandre, M. Performance evaluation of amperometric sensors for the monitoring of O₃ and NO₂ in ambient air at ppb level. *Procedia Eng.* 2015, 120, 480–483, doi:10.1016/j.proeng.2015.08.676

² Szulczyński, B.; Gębicki, J. Currently Commercially Available Chemical Sensors Employed for Detection of Volatile Organic Compounds in Outdoor and Indoor Air. *Environments* 2017, 4, 21, doi:10.3390/environments4010021

At first, an extended review of the existing commercial sensors for organics compounds measurements was carried out leading to the publication of a scientific paper “Review of portable and low-cost sensors for the ambient air monitoring of benzene and other volatile organic compounds”, L. Spinelle et al., Sensors (MDPI). Taking in consideration the target concentration of around 1.5 ppb, a set of five commercially available sensors were selected. Table 14 lists the type, the working principle of the selected devices and their limit of detection given by manufacturers. Because this low target concentration excluded almost all the sensors/sensor devices, three devices, part of other research projects, were included in the evaluation process. The first one uses a multi Metal Oxide (MOx) semiconductor gas sensor operated in Temperature Operation Cycle (TCO). The second one uses the same approach TCO but with a silicon carbide field effect transistor (SiC-FET) sensor prototype. The last one is a miniaturized Gas Chromatograph based on PID sensor.

Table 14: List of commercial benzene sensors and portable devices selected for both laboratory and field campaign given in the last 2 columns

Manufacturer/ Institute	Model	Principle	Limit of detection, ppm	Laboratory tests	Field tests
Aeroqual	VM10	MOx	0.001 (resolution 0.0001)	X	X
Alphasense	PID-AH	PID	0.0005	X	X
Airpointer	miniGC	Portable GC+PID with calibration system	0.0002		X
Ion Science	Tiger Select	Portable hand held based on PID sensor	0.010 (resolution 0.001)	X	
Membrapor	ETO/M-10	Electrochemical	resolution 0.05	X	X
Membrapor	CH2O/M-10	Electrochemical	resolution 0.01	X	X
Mocon Baseline	item 045-014	PID	0.00025	X	X
Mocon Baseline	Voc Traq	PID	0.010		X
Univ. of Saarbrücken	Not available	MOx+TCO	n. a.	X	
Univ. of Linköping	Not available	SiC-FET	<1 ppb	X	
CNR-IMM Bologna	miniGC	Portable GC + PID	0.0002	X	X

An important achievement in this part of the project was the improvement of the performances of the JRC gaseous Sensor Exposure Chamber system (gSECs) by addition of a Gas Chromatograph - Photoionization Detector (GC-PID) spectrometer 955 from Synspec and a Proton Transfer Reaction – Mass Spectrometer (PTR-MS). The GC-PID has been used to provide the reference measurements of benzene, toluene and ethyl-benzene, xylene while the PTR-MS was used in the near to real-time control of the experimental process. The GC-PID 955 also ensure selectivity, accuracy and traceability of the concentration of BTEX during the entire experimental campaign. The measurement of the levels of inorganic species was carried out by traditional analysers. All parameters (benzene and interfering gas concentrations, temperature, humidity, etc.) are automatically and independently set and controlled. Unlike other exposure chambers, the reference values of all compounds are measured allowing the full traceability to national/international units when evaluating sensors.

In a second stage, the performances of the selected sensors were evaluated experimentally in the laboratory under controlled conditions in the exposure chamber.

JRC in collaboration with REG(UdS) and VSL designed and applied a testing protocol to validate the performance of micro-sensors and calibration procedures. The testing protocol has an extensive experimental design, covering the evaluation of metrological parameters such as response time, repeatability, lack of fit of calibration with hysteresis and drifts. Meteorological interferences are also evaluated, in particular the effect of temperature, relative humidity, pressure and wind velocity. Cross sensitivity, indication of the specificity of the gas sensors, is a major test and it covers the following interfering gaseous compounds: ozone, nitrogen oxides, carbon monoxide, toluene, xylene and five low-weight alkanes.

The experimental work in the laboratory has provided preliminary results on the response time, on the hysteresis in concentration, on the influence of temperature and relative humidity and on the organic interfering compounds.

During the laboratory campaign, in particular, the response time of sensors, t_{90} , the time needed by the sensor to reach 90% of the final stable value in both increasing and decreasing concentration was evaluated. For this test, temperature and humidity were kept constant. Only one PID sensor and the MOx+TCO sensor showed a response time similar to the PTR-MS, about 6 min. The mini-GC prototype was not considered in this test as it uses a miniaturized chromatograph column with a separation time of about 15 minutes similar to the reference GC-PID 955. For the other sensors, it was not possible to determine a response time because measurements were obfuscated within noise.

Table 15: Slope and coefficient of determination of the linear regression (R^2) during the laboratory calibrations (24-08-2016) and field tests (04-01-2017)

	Slope, V/ppv	R^2	Slope, V/ppv	R^2
CH2O_1	$-9.75 \cdot 10^{-6}$	0.33	-0.456	0.01
CH2O_2	$1.14 \cdot 10^{-5}$	0.48	0.159	0.00
ETO_1	$-1.83 \cdot 10^{-4}$	0.97	-0.015	0.00
ETO_2	$-1.29 \cdot 10^{-4}$	0.95	-0.370	0.02
VM_1	$1.27 \cdot 10^{-4}$	0.98	0.961	0.89
VM_2	$1.23 \cdot 10^{-4}$	0.77	0.948	0.87
PIDAH_1	$2.01 \cdot 10^{-5}$	0.79	0.612	0.25
PIDAH_2	$7.93 \cdot 10^{-5}$	0.99	0.501	0.06
PiDTECH	$2.58 \cdot 10^{-4}$	0.99	0.117	0.00
MOx+TCO	$2.20 \cdot 10^{-3}$ a.u.	0.90		
Tiger_Select	$-2.37 \cdot 10^{-1}$ ppb	0.80		
miniGC	6.87 height/ppb	0.99	1 height/ppb	0.98
SiC-FET	$-2.14 \cdot 10^{-8}$ A/ppb	0.93		

The original calibration levels ranged between 0 to 3 ppb of benzene by steps of 0.5 ppb in randomised order to take into account any possible hysteresis effects. Generally, calibration lines were found linear. The two left columns in Table 15: Slope and coefficient of determination of the linear regression (R^2) during the laboratory calibrations (24-08-2016) and field tests (04-01-2017) give the slope and the coefficient of determination (R^2) of the most significant calibration lines. The MOx gas sensor (model VM10), the PID gas sensor (model PID-AH), the Tiger Select and the electrochemical CH₂O sensors showed low precision and large scattering of measurement data. The other sensors showed a high correlation with the reference measurements.

The effect of other interferent organic compounds such as toluene, xylene, ethane, propane, butane and pentane was evaluated. The concentration of ethane, propane, butane and pentane was estimated based on the dilution of a high concentration gas cylinder into the gaseous Sensor Exposure Chamber system (gSECs) using the continuous measurement of the different flows monitored during the experiments.

Table 16 gives the sensitivity coefficient, expressed in ppb of benzene per ppb of interfering species, with the associated combined uncertainty for all the selected sensors and for the six organic interfering species. This coefficient gives the analogue response of the sensor as benzene equivalent (except the miniGC that is able to separate BTEX) when exposed to the given concentration of interfering species. The cross sensitivity increases with the value of the coefficient, and a coefficient of 1 correspond to 100 % interference.

Table 16: Sensitivity coefficient of the sensors to organics interfering compounds in ppb of benzene per ppb of interfering. Each interfering level is given in the column header. Quoted values give combined uncertainties in ppb.

	Toluene, 1.96 ppb	m,p-Xylene, 2,5 ppb	Ethane, 11.73 ppb	Propane, 4.43 ppb	n-Butane, 3.2 ppb	n-Pentane, 2.35 ppb
CH2O_1	-1.39 ± 0.75	2.45 ± 1.71	0.34 ± 1.14	-0.58 ± 0.75	-1.87 ± 1.73	1.12 ± 0.76
CH2O_2	5.71 ± 3.08	3.03 ± 2.11	0.59 ± 2.01	0.70 ± 0.90	0.86 ± 0.79	-0.74 ± 0.50
ETO_1	3.63 ± 1.96	2.07 ± 1.44	0.10 ± 0.35	0.52 ± 0.67	0.23 ± 0.22	0.02 ± 0.01
ETO_1	3.37 ± 1.82	1.88 ± 1.31	0.02 ± 0.06	0.65 ± 0.84	0.35 ± 0.33	-0.27 ± 0.18
VM_1	0.91 ± 0.49	74.93 ± 52.21	-0.13 ± 0.44	0.80 ± 1.02	2.98 ± 2.76	-0.04 ± 0.03
VM_2	6.55 ± 3.54	-22.68 ± 15.8	-0.75 ± 2.55	0.14 ± 0.18	-8.70 ± 8.04	2.68 ± 1.82
PIDAH_1	7.08 ± 3.82	-3.64 ± 2.53	0.21 ± 0.72	-0.4 ± 0.52	1.15 ± 1.07	-0.43 ± 0.29
PIDAH_2	1.78 ± 0.96	-1.08 ± 0.75	0.08 ± 0.27	-0.22 ± 0.28	-0.88 ± 0.82	-2.47 ± 1.68
PiDTECH	0.50 ± 0.27	0.15 ± 0.10	-0.01 ± 0.05	0.10 ± 0.13	0.28 ± 0.26	0.15 ± 0.10
MOx+TCO	2.73 ± 1.47	3.52 ± 2.45	-0.14 ± 0.47	-0.10 ± 0.12	0.73 ± 0.68	0.28 ± 0.19
Tiger_Select	4.56 ± 2.46	0.21 ± 0.15	0.11 ± 0.36	1.35 ± 1.72	-2.95 ± 2.73	1.73 ± 1.17
miniGC	$5.2 \cdot 10^{-2} \pm 2.8 \cdot 10^{-2}$	$2.6 \cdot 10^{-2} \pm 1.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-4} \pm 4.8 \cdot 10^{-4}$	$-1.6 \cdot 10^{-3} \pm 2.1 \cdot 10^{-3}$	$2.6 \cdot 10^{-2} \pm 2.4 \cdot 10^{-2}$	$-1.9 \cdot 10^{-2} \pm 1.3 \cdot 10^{-2}$
SiC-FET	-0.83 ± 0.45	-0.35 ± 0.24	0.15 ± 0.51	0.11 ± 0.14	0.22 ± 0.20	-2.89 ± 1.96

In general, the sensitivity coefficients for toluene and xylene are associated with lower uncertainty than for alkanes, showing that they are likely more significant. The electrochemical sensors (CH2O/M-10 and ETO/M-10) tend to be more affected by toluene and xylene than the other alkanes. The same behaviour has been observed with the VM10 sensors though they showed a high cross-sensitivity to xylene with sensitivity coefficient of around 75 ppb/ppb and -23 ppb/ppb. The Tiger Select is affected by the whole set of tested interfering species. The two PID-AH sensors and the MOx-TCO seem to be particularly affected by toluene and xylene and slightly by butane and pentane. The mini-GC, PiDTECH and SiC-FET present the lowest interfering effect among all tested sensors. This is particularly true for the mini-GC considering that this device uses a miniaturized separation column.

The effect of inorganic compounds (ozone, nitric oxide and nitrogen dioxide and carbon monoxide), was also evaluated for some of the sensors. The most significant effect was observed for CO on the VM10 sensors ($R^2=0.99$) and to a lesser extent the MOx+TCO sensor ($R^2=0.73$). NO₂ particularly affected the MOx+TCO ($R^2=0.99$) and the two PIDAH sensors ($R^2=0.91$). The high interference of CO and NO₂ on the MOx+TCO

can be justified as this particular device uses one combined CO/NO₂ sensor as one of the multi sensor. The PIDAH sensors also have a high sensitivity to O₃ with an R²=0.87.

The hysteresis effect studied by changing the benzene concentrations showed that only the PID sensors and electrochemical cells seem to be sensitive to this effect.

The influence of the changes of temperature or relative humidity on the sensor's response were also studied. Two series of tests were conducted independently, generating ramps of temperature and humidity in a hysteresis cycle while benzene was kept constant. The ranges of temperature changed between 12 and 32 °C (by step of 5 °C) and the range of humidity was kept between 40% and 80% (by step of 10%). In general all the tested sensors showed a strong dependency on temperature and relative humidity characterised by linear and quadratic regression lines, respectively. Only the mini-GC was found without any temperature and relative humidity effects.

In conclusion, the laboratory evaluation shows that the current sensor technology is not able to accurately and selectively measure benzene at ambient levels. The PID sensors were generally found linear but they intrinsically suffer from high cross-sensitivity to other organic compounds. Amperometric and PID sensors seem also to suffer from a significant hysteresis effect. Finally, both amperometric cells and semiconductor sensors suffer from a lack of sensitivity and high dependency to relative humidity and temperature. Only the sensor based devices (mini-GC and MOx+TCO) were able to reach a reasonable sensitivity together with almost non-existent cross sensitivity towards other gaseous interfering compounds.

Finally, the set of sensors has been tested under field conditions from December 2016 to May 2017 at the JRC station for atmospheric research in a semi-rural area. The JRC station was equipped with meteorological sensors and reference gas analysers for BTEX, O₃, NO₂/NO/NO_x, CO and SO₂. In this period the JRC EMEP (European Monitoring and Evaluation Programme) station showed typical benzene levels of semi-rural stations with hourly benzene values ranging between 0.1 and 1.3 ppb and therefore limiting the sensors capability to detect such low benzene levels. Additionally, benzene was strongly correlated first with CO ($r = 0.944$) and second with BTEX and NO_x (r about 0.8). These correlations seemed to overrule the findings relative to the cross-interference effects studied in the laboratory.

Among all sensors, the mini-GC supplied by CNR - IMM Bologna showed the best performance. The relative expanded uncertainty estimated using the method of the Guide for Demonstration of Equivalence for measurement methods³ was equal to $U_r = 22\%$ at 1.4 ppb, well within the data quality objective of 30 % of relative expanded uncertainty at 1.5 ppb of benzene.

Among all other sensor tested in field, only the Aeroqual VM10 sensors presented linear calibrations with a decent coefficient of determination, R², of 0.89. However, it was found that this sensor was affected by a strong CO interference while the laboratory tests showed poor calibration with benzene. It is thought that the good results obtained with the VM10 for the sole field test are in fact the consequence of the CO interference rather than from benzene measurements. For the rest of the sensors, the coefficient of determination R² were all found lower than 0.25, preventing from using these sensors for any field benzene measurements. Chemical and PID sensors did not give suitable results at low level of BTEX with benzene lower than 1.5 ppb, for lack of sensitivity of the chemical sensor and lack of selectivity of the PID sensors.

3.5 Collaborations between the project partners

All technical and dissemination activities have been successfully completed thanks to the commitment and contributions of all KEY-VOCs partners and REGs. By joining these capabilities together, the European project partners and REGs could deliver a metrologically sound answer to the VOC surface adsorption problem and to the other challenges expressed by the VOC European and International VOC measurement community.

³ Report by EC Working Group on Guidance Guide to the demonstration of equivalence of ambient air monitoring methods; 2010

Good example of collaboration from the beginning of the project was the measurement of VOC impurities in zero gases and the evaluation of the performance of purifiers carried out by REG(DWD), INRIM and VSL jointly.

Also, the work on the development of polar-VOCs for indoor air measurements could not be successful if INRIM and TUBITAK would not have worked together. In this case, the preparation of the transfer standards in sorbent tubes was done at INRIM, while the analysis of the standards and the stability testing was carried out at TUBITAK using the IDMS method developed in the project.

The two comparisons on standards for atmospheric monitoring and indoor air were another good example of joint research is the performance in preparing gas standards and the measurement capabilities developed by the partners were planned, evaluated and discussed together.

The collaborative research between partners and REGs has led to the submission and publication of several joint-papers dealing with zero gases, with novel devices for dynamic methods, with reproducibly emitting materials for indoor air and with validation of VOC gas sensors.

The collaboration, in the form of knowledge transfer or knowledge sharing, was a key aspect of the project. Regular plenary sessions for project partners and dedicated partner-to-partner (or REG) trainings were held in order to share experience, know-how and these events were a good moment to strengthen on-going collaboration and discuss potential new research activities for the future. Good example was the two-day training of REG(DWD) at VSL in the framework of the activities in atmospheric monitoring where the experience of measuring VOCs in the field (REG(DWD) is an experienced WMO GAW station) and the metrological aspects discussed in the lab. Another example was the transfer of knowledge where NPL provided support to CMI in solving the preparation and analysis problems they were facing in the preparation of OVOC gas standards.

The organisation of the KEY-VOCs Webinar as conclusion of the project activities has been a very good example of cooperation in the last six months, where all project members had an intensive brainstorm and provided their inputs to INRIM the webinar organiser. Finally, the webinar was a success and the presentations are available on INRIM website.

It must be noted that this research project received also very good support from the collaborators such as Restek, Air Liquide, Linde, Air Products, Takachiho and Gradko, who contributed to the project success by delivering gas cylinders and analytical parts for testing and complementary measurement data.

3.6 Summary

- Important new and first-in-the-world knowledge has been gained by REG(DWD), VSL, NPL, LNE, INRIM and REG(POLITO) on passivation methods suitable for the preparation of stable VOC standards at trace levels (ppb) and for the measurement of challenging reactive VOCs such as alcohols and aldehydes. This knowledge has been disseminated at various events to the scientific community. It is expected to be used by NMIs/DIs for preparation of their own gas standards by static and dynamic methods, by the atmospheric and air monitoring networks for the choice of the material used in their measurement set-up and by the coating industry to further promote and improve their technologies.
- A new measurement capability in the laboratory of PTB has been established thanks to the development of a “novel in situ gas cell” that allows the measurement of gas sorption behaviour at surfaces by total reflection X-ray fluorescence analysis. PTB operates several beamlines at the synchrotron radiation facility BESSY II and it provides measurement services to and collaboration projects with industry and other research groups.
- An improved “Certification Protocol for Zero Gases” (originally developed in the EMRP project ENV01 MACPoll for inorganic air pollutants) for the determination of ultra-low (ppt) concentrations of VOC impurities in zero gases has been developed. This protocol, validated by REG(DWD), INRIM and VSL, has been used as input in the revision of the ISO 19229 “Gas analysis - purity analysis and the treatment of purity data”.
- New Research Gas Mixtures for OVOCs in pressurised cylinders have been developed by VSL for methanol, ethanol, acetone, MEK, MVK, methacrolein and acetaldehyde at 100 nmol/mol. These traceable gas standards are available for the atmospheric monitoring and air quality networks for the calibration of their instrumentation.
- New reference gas standards for monoterpenes at 2-4 nmol/mol have been developed as first in Europe by NPL and they are intended for use in the calibration of instrumentation of atmospheric monitoring stations.
- Improved knowledge and experience has been gained by LNE and NPL in the preparation of formaldehyde gas standards at 1 µmol/mol by static and dynamic methods. This know-how is intended for the certification of gas mixtures of air monitoring networks and gas manufacturers.
- Two portable gas generators were designed and constructed by METAS and INRIM. The ReGas2 (METAS), based on the permeation method, and the INRIM generator, based on the diffusion method, are now validated. They are available for field calibration of instrumentation both in outdoor air monitoring and in specific applications where VOC measurements are needed, such as for breath analysis in hospitals.
- New gas standards and transfer standards in tubes for indoor air quality are now validated by INRIM and VSL for respectively polar- and semi-VOCs. These standards are intended for QA/QC of the analytical measurements performed by emission testing and indoor air laboratories.
- New reference material with characterised emitting behaviour is available at BAM. This material mimics the emissions of a real construction product test sample and it is intended for validation and QA/QC of the test chamber methods used by emission testing laboratories.
- New validation protocol and calibration procedures for (micro) gas sensors and miniaturised gas devices intended as indicative methods in the measurement of benzene in air have been developed by JRC, in collaboration with REG(UdS) and VSL. These procedures are now available and they are currently used as input for the drafting of Technical Specifications “Air quality – Performance evaluation of air quality sensors”. By doing this, gas sensor manufacturers and testing institutes can make use of the project outputs.
- A gaseous Sensor Exposure Chamber system (gSECs) has been optimised by JRC for the measurement of VOCs. The equipment is in use for the validation of gas sensors.
- Important, new and certainly first-in-the-Europe knowledge has been gained by JRC, REG(UdS) and VSL in better understanding of the influencing factors, performance and uncertainty of the (micro) gas sensors available on the EU market. This knowledge is captured in open access publications.

4 Actual and potential impact

4.1 Dissemination activities

The project partners aimed at creating impact by use of conventional and modern dissemination methods. On one hand, participation at conferences and scientific publications guaranteed the uptake of the JRP outcome by researchers and experts in the field. On the other hand, the website and the creation of a social network aimed at reaching a larger group of people not necessarily VOC experts.

4.1.1 Website and social network

The website (www.key-vocs.eu) was developed and managed by VSL. It contains a description of the project activities, consortium and project outcome. This website has been regularly updated to include the last news of the project and dissemination material.

In order to enhance the interaction with end users, the project consortium created a LinkedIn group called "VOC Measurements". This group has been regularly posted and it will remain active in order quickly disseminate the project results and VOC related issues beyond the end of the project. At the end of the JRP the group consists of 126 members.

4.1.2 Scientific publications

This project has generated 13 peer reviewed publications, of which 11 have been published and one PhD thesis.

4.1.3 Presentations at conferences

The project's activities and results have been widely disseminated in targeted scientific events such as GAS Analysis, EGU, Indoor Air and SENSOR and in events for a broader audience such as the Int. Congress of Metrology and Pittcon. In total 36 oral presentations and 18 posters presentations were given by the project partners and grant researchers at conferences, workshops and seminars. KEY-VOCs project results are still being presented after the end of the project.

The poster "Development of Oxygenated VOC gas standards to underpin atmospheric monitoring", A. Baldan, J. Li, S. Persijn (VSL) was awarded by the organisation of the Gas Analysis Symposium and exhibition 2017 (the Netherlands) as the "best conference poster".

4.1.4 Organisation of project events

During the project, a stakeholders' mid-term meeting organised at LNE (F), two workshops, respectively indoor air organised by BAM (D) and gas sensors organised by JRC (I), and a final Webinar, organised and hosted by INRIM (I), were held between April 2016 and September 2017. In total, 17 lectures related to the project activities and results have been given. All these events were well-received and provided excellent interaction opportunities with stakeholders and end-users. To make the events even more interesting, scientific experts, stakeholders and collaborators of project were invited to give a presentation.

For example, the following experts represent a selection of the invited speakers:

- for the stakeholders' mid-term meeting, the responsible for the WMO GAW World Calibration Centre for VOCs and a scientific staff of Bureau International des Poids et Mesures (BIPM) involved in gas analysis
- for the workshop on gas sensors two project collaborators from Linköping University (S) and CNR-IMM (I)
- for the workshop on indoor air, the director of eco-INSTITUT, a German emission testing laboratory.



Figure 19: Overview of KEY-VOCs project events. Left, participants to the Stakeholders Mid-Term meeting; right up, presentation at the workshop on indoor air; right down, demonstration at the workshop on gas sensors.

The Webinar was held on the 5th of September 2017 and it was divided into three sessions: Atmospheric monitoring, Indoor Air and Gas sensors. Each session consisted of several presentations and a round table discussion. During the discussion, examples were shown of project results applications. The word was therefore given to industrial collaborators, such as the industrial manufacturer of material coatings (SilcoTek) and to end users such as an emission testing laboratory (Eurofins) and an institute dealing with culture heritage protection (Venaria Reale). In total, there were 67 attendees from which 38% came from private companies and 15% from universities. Lots of positive feedback was received from the participants via a questionnaire sent out directly after the event.

4.1.5 Organisation of trainings

An important objective of this project consisted of making sure that the knowledge acquired by the partners in the project was also shared. For this reason, seven trainings were given by project partners and grant researchers in occasion of the plenary meetings. Several dedicated trainings were also given to stakeholders and users, such as students from academia, scientists of other NMIs (e.g. Singapore) and industrial collaborators (e.g. Fine Metrology).

4.1.6 Engagement with standardisation

This project has been interacting with CEN/TC264/WG42 “gas sensors” where Michel Gerboles (JRC) is the chair and VSL, NPL and LNE are members. This WG, made up of EU experts from industry, research, metrology and type testing, is developing a Technical Specification (TS) “Air quality – Performance evaluation of air quality sensors”. The protocol of gas sensor validation developed in this project has contributed to the drafting of the TS. At the last meeting, in October 2017 (just after the end of the project) it was decided to submit a project proposal in order to change the Technical Specification in development into a draft documentary standard.

The project partners engaged with other standardisation technical committees dealing with gas analysis, air quality and X-Ray techniques at international, European and national level, namely ISO/TC158, ISO/TC201/SC10, CEN/TC264/WG12, DIN NA062-08-16 AA and NEN 390050. The project activities and (where possible) the results were presented at the meetings.

4.1.7 Engagement with stakeholders

The engagement with the atmospheric monitoring community was ensured by the participation to two WMO GAW VOC network workshops of REG(DWD) (Hohenpeissenberg Observatory), NPL and VSL. The first event was organised in October 2014 and held at KRISS in South Korea. During this event, the project was introduced to the network and a priority list of key VOCs relevant in atmospheric monitoring and climate

change was selected to be further investigated in the project. The second event was in May 2017 at INSTAAR, University of Colorado, Boulder (USA) and it was an excellent opportunity to present the project results to the WMO GAW stations. During this event, 2 posters and 2 oral lectures were given.

These results, namely the developed calibration gases for the VOC priority list, the zero gas verification and the outcome of the VOC adsorption characterisation studies, were also presented and discussed at the ACTRIS meetings by REG(DWD) (member of the EU ACTRIS project) attended by EU EMEP stations and Meteorological institutes.

The engagement with the EU Air quality network (AQUILA) was mainly ensured by JRC. This partner introduced the project and the progress in gas sensor evaluation activities at the network meetings. The interaction with the indoor air community occurred at the begin of the project, when the selection of the key VOCs indoor air components was made in collaboration with AgBB and towards the end at the KEY-VOCs workshop on Indoor air, where the main EU emission testing laboratories participated.

4.2 Early impacts

- The two portable calibrators (dynamic gas generators) have been used for the calibration of instrumentation in the field for air monitoring (at the Swiss and Italian monitoring stations) and health applications (for breath analysis in hospitals). These prototypes have the advantage of being flexible in the generation of gas concentrations and, if proven to be robust and easy to use, they will be a valid option for use in the field. An interesting spin off, the ReGas2 portable generator, will be commercialised in the short-term future.
- The project findings have been used by IAGOS-CARIBIC (European Infrastructure for using passenger aircrafts for Global Atmospheric Observations - Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) project members, who perform particle and trace gas measurements, including VOCs, on board of commercial aircrafts. The project adsorption studies have been used for the selection and characterisation of the tubing material for the inlet system of a new container set-up.
- A new in-situ gas cell measurement capability is now established at PTB, and available for industry, metrology and research institutes.
- LNE performed calibrations on a formaldehyde cylinder to certify the amount fraction of the gas mixture, for the company Air Liquide, ensuring traceability to French national reference standards.
- ACTRIS and GAW laboratories are currently making use of one of the OVOCs transfer standards, developed in this project, to perform a parallel round-robin exercise. These traceable gas standards, developed for the atmospheric monitoring community, will be used by these laboratories for calibrations in the near and long- term.

Contribution to standards

The reproducibly emitting reference material and the gas transfer standards developed in the KEY-VOCs project for indoor air and emission testing measurements are set to be used for a joined Proficiency Testing (PT) planned for 2018. The objective is to evaluate the proficiency in measuring VOC and SVOC according to EN 16516 "Construction products: Assessment of release of dangerous substances - Determination of emissions into indoor air" and to ISO 16000 parts 6 and 9 (dealing with measurement of VOC in indoor air). Thanks to this material and these standards, it is now possible to ensure quality assurance and quality control (QA/QC) of the measurement systems used in indoor air monitoring and the proper implementation of indoor air documentary standards so that the compliance with the Construction Products Directive and Regulation is guaranteed and the risk of indoor pollutants in buildings is minimised.

This project was also engaging with the recently formed CEN/TC264/WG42 "gas sensors". The validation protocol for gas sensors developed in this project has fed the drafting of the Technical Specifications "Air quality – Performance evaluation of air quality sensors".

Project outputs, such as the verification of zero gases, have been included in the WMO guideline for Non Methane Hydrocarbons, meaning that they will be used by the global network of stations. In the long-term it is expected that all GAW stations worldwide will meet the challenging Data Quality Objectives for the priority reactive VOCs and therefore they will produce reliable long-term data, essential for a better understanding of the global trends in atmospheric monitoring and in climate change

4.3 Longer-term impacts

In the longer-term it is expected that the coating industry will make use of project results for the development of new passivation technologies that lead to new inert materials.

Air monitoring networks and environmental authorities have benefitted from the project's gas sensor results and from the validation protocol and calibration procedures developed. This information gives guidance on the state-of-the-art in VOC gas sensing and helps end-users and policy makers to understand the pros and cons of these sensor devices when applied in the field.

In the longer-term, when gas sensor performances are successfully demonstrated, the devices will represent a new way to monitor air, following the EU Air Quality Directive (2008/50/EC), with the additional advantages of being low-cost, providing real-time data and a large space coverage.

5 Website address and contact details

Project website address <http://www.key-vocs.eu/>

After registration, the download area of the website becomes accessible and important public project outputs are freely available.

LinkedIn Group VOC Measurements

<https://www.linkedin.com/groups/8249987>

Contact details

For further information on the project, contact Mrs. Annarita Baldan, VSL (ABaldan@vsl.nl).

For information on adsorption studies on surfaces and certification of zero gas, contact Mr. Stefan Persijn, VSL (SPersijn@vsl.nl).

For information on gas standards for atmospheric monitoring, contact Mr. Dave Worton, NPL (dave.worton@npl.co.uk).

For information on transfer standards for polar and SVOC in indoor air and reproducibly emitting materials for quality assurance purposes, contact Mr. Matthias Richter, BAM, (matthias.richter@bam.de).

For information on VOC gas sensors for air quality measurements, contact Mr. Michel Gerboles (michel.gerboles@jrc.ec.europa.eu).

6 List of publications

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