Overview

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.

Need for the project

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. However, prior to this project it was difficult to accurately measure and compare the data of global, European and national networks dealing with key VOCs in air pollution and climate change.

Sampling and analytical methods of trace level (part-per-billion to part-per-trillion) VOCs in air were available 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.

There was a need for work looking at the VOC key compounds (indicators) that are regulated by the European legislation, that are relevant for indoor air monitoring and for air quality and climate monitoring programmes like the VOC programme established by the World Meteorological Organization (WMO) – Global Atmosphere Watch (GAW) and the UNECE's European Monitoring and Evaluation Programme (EMEP).

WMO/GAW has set challenging Data Quality Objectives in terms of uncertainty of measurement data for the atmospheric monitoring programmes. The priorities of the GAW VOC network are set to oxygenated-VOCs (OVOC), oxidation products from anthropogenic and biogenic origin and to terpenes, biogenic aerosol precursors. Prior to the project for these classes of VOCs, traceable and stable gas standards were still lacking. There was therefore a need to develop fit-for-purpose gas standards based on novel passivation chemistries to guarantee mixture stability and improved preparation methods. There was also a need for standards for reactive VOCs that are not stable in high-pressure gas cylinders.

Measuring VOCs is complex because of their variety, their different physical and chemical properties and their presence in the atmosphere at very low concentration levels. Currently, more than 15 documentary standards on VOCs are published or in preparation by European (CEN TC 264 ‘Air Quality’) and International (ISO/TC
146 ‘Air Quality’, ISO/TC 158 ‘Gas Analysis’) standardisation committees to cope with the need of measuring different VOCs gaseous species respective of the application and concentration levels. To support their implementation an improved metrological infrastructure was necessary, to provide traceability to the measurement results and reference materials, for the quality assurance and quality control (QA/QC) of the measurement systems.

In addition, there was a need to develop high spatial resolution measurements to understand ambient concentration patterns with respect to requirements of the EU Air Quality directive (2008/50/EC), including benzene, a harmful air pollutant. This part of the project builds on the measurement protocol developed in project ENV01 Metrology for chemical pollutants in air.

Scientific and technical objectives
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.

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).

4. Validation of measurement standards and measurement systems
   • Validate the measurement gas standards developed in objectives 2 and 3 by organisation of a comparison among the project partners.
   • 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.
Results

The results of the research on the physical and chemical interactions between VOCs and contact surfaces and of the testing of measuring and purification techniques for VOC-free zero gases were paramount to the final outcome of the project: the development of accurate and stable VOCs reference standards and the validation of novel VOC calibration systems. This outcome has contributed to provide the metrological tools so that the European and global VOC measuring community in atmospheric monitoring, air quality and indoor air can reach the target uncertainties and meet the traceability requirements. The development of a validation protocol for low-cost VOC sensing devices and the evaluation of a selection of these sensors have provided a better understanding of the reliability of these devices and technologies, stimulating therefore their technological improvement.

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

The interaction of methanol with surfaces, such as the tubing used for gas sampling lines, was investigated. Different types of materials were tested at VSL and DWD: coated and uncoated stainless steel, nickel, brass, copper, aluminium and polymeric surfaces such as PTFE. Adsorption studies were carried out on methanol vapours at low concentrations (ppm-ppb range). A Cavity Enhanced Absorption Spectroscopy (operating at 9.5 µm), a Cavity Ring-Down Spectroscopy spectrometer (that can assess all lines in the 3.2-3.6 µm range) and a Flame Ionisation Detector system were used. The test results indicate that methanol adsorbs (adheres) strongly on surfaces, but the adsorption is less significant than other reactive gases such as ammonia (which was studied in project ENV01). The adsorption by most polymers such as PTFE and FEP is extremely low, while for uncoated metals it is very high. Coated stainless steel with Silconert-2000 and Sulfinert are the preferred choice, as they also have the benefit of being robust non-permeating materials. The synchrotron radiation facility BESSY II was used by PTB to perform the analysis of gas species adsorbed on coated and uncoated metal surfaces. A novel ‘in situ gas cell’ that allows the measurement of gas sorption behaviour at surfaces by total reflection X-ray fluorescence analysis was developed.

In order to understand the effect of leakages and of surface interaction in dynamic generation systems for oxygenated Volatile Organic Compounds (OVOCs), a study was carried out at INRIM using acetone as the target VOC. A model describing these effects was developed and validated by POLITO, and makes it possible to evaluate new coating technologies, new materials and the associated uncertainty.

Analytical methods were developed for the evaluation of trace VOC impurities in zero gases and were metrologically validated to be able to assess ultra-low levels (few ppt). This has allowed, for the first time, the desired levels of detection for most of the anthropogenic, biogenic and oxygenated VOCs. The performance of purifiers supplied by two collaborators for the removal of VOCs was evaluated and included in the WMO Guideline for measuring Non Methane Hydrocarbons.

2. Reference standards to underpin atmospheric monitoring of VOCs

At the start of the project, the partners working with the WMO-GAW, identified the priority compounds for which reference standards were necessary. This set of priority compounds included OVOCs, formaldehyde and monoterpenes.

Feasibility studies were performed by NPL, LNE and VSL to evaluate the suitability of preparing reference gas standards with the required level of accuracy by gravimetry (static method). Different types of cylinders were tested and showed that alcohols (methanol and ethanol) more than other OVOCs have a significant loss when prepared in aluminium cylinders and therefore this loss should be taken into account when assigning the reference value to the gas mixture. This loss appears to be insignificant for stainless steel Silconert coated cylinders. The most suitable cylinders were used for the preparation of the gas standards at trace levels, respectively 100 nmol/mol and 1 µmol/mol for up to 7 OVOCs, 1 µmol/mol for formaldehyde and 2 nmol/mol for monoterpenes. Long-term studies up to 19 months have shown that for some components, such as formaldehyde, methanol and possibly some monoterpenes species, it is difficult to prove stability of the gas concentrations over time. In conclusion, acetone, methyl ethyl ketone (MEK), methyl vinyl ketone (MVK) and methacrolein static gas standards at low amount fractions comply with the atmospheric monitoring Data Quality Objectives of 5 % expanded uncertainty. For the other components (methanol, ethanol and acetaldehyde), further stability studies or new cylinder passivation technologies will be needed to revise the uncertainty budgets and ensure the long-term shelf life of the gas standards.
Two portable gas calibrators were designed and built by METAS and INRIM, and were able to generate well characterised and reproducible gas concentrations of VOCs at trace levels. The METAS portable gas generator, the ReGas2, is based on the permeation method (dynamic preparation technique) and it allows the simultaneous generation of several VOC gas mixtures. It was validated for the generation of ethanol, MVK and limonene. INRIM portable VOC based on the diffusion method (another type of dynamic preparation technique), produces gas mixtures at ppb level of oxygenated compounds was validated for methanol, ethanol and acetone.

3. Development of VOC gas standards for indoor air measurements

At the beginning of the project, the partners in collaboration with the German Health Evaluation of Building Products Committee (AgBB), selected a number of VOC components relevant for the quality control and quality assurance (QA/QC) of emission measurements from construction products. This included polar-VOC (pVOC) like acetic acid and semi-VOC (SVOC – a subgroup of VOCs that tend to have a higher molecular weight and higher boiling temperature, and are abundant in indoor air) such as D6 cyclic siloxane.

The generation of pVOC was carried out at INRIM with a dynamic generation system based on diffusion method. pVOC transfer standards in sorbent tubes were obtained by pumping known volumes of gas into the tubes. This preparation method led to an expanded uncertainty ranging from 4 to 5 %. The generation of the SVOC using a new VSL design was able to achieve trace concentration levels using a two-stage dynamic dilution technique. The performance of this system was validated with n-decane, which was successfully generated at trace levels (ppb) and trapped in sorbent tubes (transfer standards) with an expanded uncertainty of around 2 %. The less volatile components were generated and trapped in sorbent tubes with an expanded uncertainty ranging from 5 – 7 %.

A research study was undertaken, to evaluate the best suitable sorbent materials for both pVOCs and SVOCs, and the safe storage period. While for SVOC the best suitable material is Tenax TA, preferably packed in coated Silicosteel stainless steel tubes, for pVOC the main challenge lies on the very limited storage period (two weeks) that can be slightly enhanced by keeping the transfer standards in the freezer.

The Isotopic Dilution Mass Spectrometry (IDMS) method for the pVOCs and the SVOCs trapped in sorbent tubes in very low amounts (ng) was successfully developed and validated at TUBITAK. Three polar-VOCs and six SVOCs were selected. This method was also used to validate the VOC transfer standards prepared at INRIM and VSL.

VOC emitting reference materials were designed at BAM in collaboration with UdS to mimic the behaviour of real emissions from construction products. These materials are important for the QA/QC of VOC emission measurements in chambers. The objective of this study was successfully realised: a thermoplastic polyurethane (TPU) 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 tested for texanol, chosen as a VOC with a comparatively low volatility. However, some of the results were indicative, and there are still some aspects which require further investigation, for example the transfer of the impregnation conditions to other VOCs and impregnation with solid compounds such as 2,6-diisopropynaphthalene (DIPN).

4. Validation of measurement standards and measurement systems

Two comparison exercises were organised to validate the measurement standards developed to underpin atmospheric monitoring and indoor air.

In parallel with the comparison to validate reference gas standards for atmospheric monitoring, a round-robin exercise was organised by the EU EMEP and GAW laboratories (under the European Research Infrastructure for the observation of Aerosol, Clouds and Trace gases, the ACTRIS project) so that one OVOC gas mixture containing 7 components at 100 nmol/mol was sent around for analysis. This exercise is still running. Good comparability was demonstrated for acetone gravimetric standards and for ethanol standards based on dynamic permeation and on gravimetry methods followed by correction for ethanol losses. The good agreement, within uncertainties, for formaldehyde results is encouraging, considering the challenging nature of this compound. The project comparison results, however, show that for other VOCs the degree of comparability is not satisfactory and that there is need for further investigation. Finally, the preliminary results of the comparison with two ACTRIS laboratories, show that there is good agreement, within uncertainties, for the seven measured VOCs with respect to the reference concentration values.
For the validation of the pVOC and SVOC gas standards developed to underpin indoor air quality and more specifically emission testing, Tenax TA sorbent tubes were loaded with both component groups. Three project partners and two collaborators took part in the comparison. Only the results from one collaborator could be taken into consideration for the evaluation. For SVOCs most of the participants successfully measured decane, Dodecamethylcyclohexasiloxane (D6), butylated hydroxytoluene (BHT), hexadecane, octadecane, eicosane and dibutylphthalate. In general, results show consistency with the reference value within the associated uncertainty. With exception of one participant, also the results of naphthalene are satisfactory. For pVOCs, participants show inconsistent results for most of the sorbent tubes loaded with butanol, hexanal, acetic acid and cyclopentanone. For isopropanol, 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.

A literature review on the availability and suitability of commercial and research-based VOC gas sensors and portable devices for air monitoring and in particular for the measurement of benzene was conducted at the start of the project. Because only few commercial systems were able to reach the required specifications (e.g. low detection levels, gas selectivity), the review was extended to devices that are in “advanced research state” and ready to be tested in this project. The results of the review have been published. A validation protocol and calibration procedures for gas sensors intended as indicative methods (Air Quality Directive) in the measurement of benzene in air were developed by JRC, in collaboration with UdS and VSL. This included characterising the response time, repeatability, lack of fit of calibration, drifts, meteorological interferences (temperature, relative humidity, pressure and wind velocity) and cross-sensitivity. This protocol was used to perform the evaluation of the selected gas sensors devices. The measurement set-up at JRC was designed and optimised by complementing the in-house gaseous Sensor Exposure Chamber system (gSECs) with a Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) - a rapid online VOC measuring device. In addition, a complex VOC dynamic calibration system was installed for the calibration and interference testing of the gas sensors. The laboratory evaluation showed that current sensor technology is not able to accurately and selectively measure benzene at ambient levels. The Photoionisation Detector (PID) type sensors were generally found linear for the measurement of benzene air concentration levels, but they intrinsically suffer from high cross-sensitivity to other organic compounds. Amperometric and PID type sensors seem also to suffer from a significant hysteresis effect. Finally, both amperometric cells and semiconductor type sensors suffer from a lack of sensitivity and high dependency to relative humidity and temperature. Only the sensor based devices, namely the miniaturised Gas Chromatograph (miniGC) and multi metal oxide/semiconductor type sensor operated in Temperature Operation Cycle (MOx+TCO) were able to reach a reasonable sensitivity together with almost non-existent cross-sensitivity towards other gaseous interfering compounds. The 5 months field campaign carried out at the EMEP air monitoring station located at the JRC concluded the experimental validation work. Among all sensors, the miniGC showed the best performance. The relative expanded uncertainty estimated using the method of the Guide for Demonstration of Equivalence for measurement methods was equal to Ur= 22 % at 1.4 ppb, well within the data quality objective of 30 % set by the Air Quality Directive for indicative benzene measurements. The other VOC gas sensors failed the validation due to poor sensitivity or specificity.

**Actual and potential impact**

**Dissemination**

The work of the project was supported by a Stakeholder Committee representing ambient air monitoring networks, atmospheric processing monitoring networks, emission testing labs, EU environmental policy makers, material testing and gas sensors experts.

Project events organised for stakeholders and collaborators included stakeholders meetings, workshops on Gas Sensors and on Indoor Air, and a one-day webinar to present and discuss the project results and the impact created.

The participants of the GAWTEC Training course ‘What we learned so far from the KEY-VOCs project’ work at GAW stations worldwide and use knowledge gained in the project for their measurements of atmospheric VOCs.
42 presentations were given at international, European and national conferences and ad-hoc meetings including Gas 2015 & 2017, IMEKO World Congress, Indoor Air 2016 and Eurosensors 2017.

The consortium liaised with networks and other projects, specifically with the European Reference laboratories for Air Quality (AQUILA), the European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability (EuNetAir), the climate monitoring networks WMO-GAW and European Research Infrastructure for the observation of Aerosol, Clouds, and Trace gases (ACTRIS-2).

Fourteen publications were published, or submitted to be published, during the lifetime of the project in journals such as Measurement, Building and Environment, Measurement Science and Technology, Air Quality Atmosphere and Health.

**Early impact**

- 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.

Future potential impact

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 leading 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.

List of Publications


| JRP start date and duration: | 1 October 2014, 36 months |
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- **JRP-Partner 3:** CMI, Czech Republic
- **JRP-Partner 4:** INRIM, Italy
- **JRP-Partner 5:** JRC, European Commission
- **JRP-Partner 6:** LNE, France
- **JRP-Partner 7:** METAS, Switzerland
- **JRP-Partner 8:** NPL, United Kingdom
- **JRP-Partner 9:** PTB, Germany
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