

FINAL PUBLISHABLE REPORT

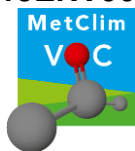
Grant Agreement number 19ENV06
 Project short name MetClimVOC
 Project full title Metrology for climate relevant volatile organic compounds

Project start date and duration:		1 June 2020, 36 months
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Internal Funded Partners:	External Funded Partners:	Unfunded Partners:
1. METAS, Switzerland	7. DWD, Germany	-
2. FMI, Finland	8. Empa, Switzerland	
3. LNE, France	9. IMTelecom, France	
4. PTB, Germany	10. KIT, Germany	
5. TUBITAK, Türkiye	11. POLITO, Italy	
6. VSL, Netherlands	12. UoL, United Kingdom	
	13. UU, Netherlands	
RMG: -		



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1 Overview

Volatile organic compounds (VOCs), as ozone and aerosol precursors, play an important role in the oxidative capacity of the lower atmosphere and contribute to radiative forcing. Thus, long-term, accurate and traceable VOC measurements are pivotal to understanding changes in climate and their effects on environment and society. However, VOC low atmospheric amount-of-substance fractions, their reactivity and the lack of stable and traceable standards for some VOCs make their sampling, analysis and calibration challenging. Within this project, stable reference gas mixtures of priority oxygenated and halogenated VOCs were produced at low amount-of-substance fractions and uncertainties (≤ 100 nmol/mol, ≤ 5 % expanded uncertainty and at least 18 months temporal stability). For some VOCs, this was the first time that stable and traceable standards were produced. Furthermore, the project provided well-characterised sampling and analytical methods and SI-traceable spectral parameters for spectrum-based techniques. Moreover, the project provided a user-friendly on-line tool to calculate uncertainties, guidelines and training on metrological aspects to monitoring stations. In addition, this project reinforced the collaboration between two communities (i.e. metrology and atmospheric research) that are crucial to ensure the comparability and quality of atmospheric data. These outputs contributed to address some of the main needs of atmospheric stakeholders.

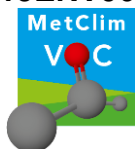
2 Need

The WMO-GCOS (Global Climate Observing System) defined 55 essential climate variables (ECV) that contribute critically to the characterisation of the Earth's climate. VOCs are designated as ECV in the categories "aerosol and ozone precursors" (oxygenated VOCs and terpenes in this project) and "carbon dioxide, methane and other greenhouse gases" (halogenated compounds in this project). VOCs are regulated by the European Air Quality Directive 2008/50/EC and emission ceilings for air pollutants defined in the directive (NEC) 2001/81/EC, which includes VOCs as ozone precursors. For the halogenated gases, which are direct greenhouse gases, fluorinated halocarbons are regulated in the regulation (EU) No 517/2014 (F-gas regulation). Furthermore, the Kyoto Protocol, developed under the United Nations Framework Convention on Climate Change (UNFCCC), obligates member states to report emissions of these greenhouse gases. Recently, these fluorinated halocarbons have been included into the Kigali Amendment of the Montreal Protocol, which already restricts the use of chlorinated and brominated halocarbons, as they destroy the ozone layer.

To control the effectiveness of these treaties and to assess climate and air quality trends, the amount-of-substance fractions of these compounds needed to be monitored. Stable traceable references with a low uncertainty along with well-defined measuring methods are indispensable for reliable VOC measurements. The WMO-GAW, the European Monitoring and Evaluation Programme (EMEP), research infrastructures (e.g. ACTRIS, AGAGE) and national air pollution networks included VOCs in their long-term monitoring programs. WMO-GAW or ACTRIS for instance, defined data quality objectives on the final measurement (ACTRIS: < 10 %). However, measuring atmospheric VOCs is challenging because they occur at very low amount-of-substance fractions (pmol/mol to nmol/mol level). In addition, some of these compounds are highly reactive and are prone to adsorption effects on surfaces, which makes the calibration of analysers, sampling and field measurements difficult. For some VOCs, there were no references available to ensure traceability and uncertainty. Finally, remote sensing methods, which show high potential to avoid sampling issues, were missing SI-traceable spectral parameters.

Significant progress has been made to improve the accuracy of VOC measurements during the past years, e.g. new traceable reference gas mixtures were established and mobile dynamic reference gas generators were developed (EMRP JRs ENV56 KEY-VOCS and ENV52 HIGHGAS); new coatings for tubing and fittings that minimise adsorption and desorption effects are available on the market. Despite this progress, some DQOs had not been met yet for all specified VOCs. This fact is underpinned by the WMO-GAW implementation plan 2016–2023, which states, as a key activity, that "uncertainty calculation" and "full traceability to the primary standard" for all measurements reported is needed.

The project contributed to some extent to meeting the DQOs by developing novel, stable and traceable references for VOCs (objective 1), improving sampling and analytical methods (objective 3), establishing guidelines and procedures for the correct sampling, calibration and analysis of VOCs (objectives 2, 3), along with the dissemination of metrological concepts (e.g. traceability of working standards, calibration and measurement uncertainty) to the field monitoring stations (objectives 2, 3, 4).



3 Objectives

The overall objective of the project was to provide and improve reference gas standards for oxygenated VOCs, terpenes and halogenated VOCs with a high focus on the dissemination of these standards to ensure the metrological traceability to the working standards and their use in the field. The measurement techniques were also validated to ensure SI-traceable measurements with a realistic and complete uncertainty budget. Assessing the major influencing factors of the measurement results and incorporating them in the uncertainty budget enabled the consortium to fulfil the objectives of data quality as specified by the corresponding measuring networks.

The specific objectives of the project were:

1. To select relevant gas compounds (oxy-VOCs, terpenes, halogenated VOCs) and to clarify the overall measurement uncertainty needed in close collaboration with stakeholders (ACTRIS and WMO-GAW monitoring networks). In addition, to develop new primary Reference Gas Mixtures (RGMs) at amount of substance fractions between 1 nmol/mol and 1 μ mol/mol (expanded uncertainty < 5 %) for oxy-VOCs and terpenes and < 1 nmol/mol (expanded uncertainty < 3 %) for halogenated VOCs.
2. To define and select fit-for-purpose protocols for the preparation of working standards that ensure an unbroken SI-traceable calibration chain for oxy-VOCs, terpenes and halogenated VOCs. In addition to validate these protocols (proof of concept) and to compare them with field calibration protocols as well as calculating the uncertainty budget for each protocol following the principles of GUM (ISO 1995) and taking into account other uncertainty sources on-site (e.g. water removal). To provide a homogenous tool for uncertainty calculation for end-users.
3. To evaluate the sampling methods for the on-line/off-line in-situ analytical measurement of the selected gas compounds and to assess relevant influence parameters. In addition, to evaluate and improve the on-line/off-line in-situ analytical methods. To determine spectral molecular parameters for spectroscopic techniques, used in remote sensing methods to assess VOCs, with SI-traceability and contribute these to the HITRAN database. To establish an uncertainty budget for the selected measurement methods.
4. To facilitate the take up of the technology and measurement infrastructure developed in the project by: the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (CEN, Air Quality directive NEC 2001/81/EC) and end users (e.g. WMO-GAW, EMEP, ACTRIS, AGAGE and AQUILA).

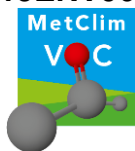
4 Results

4.1 To select relevant gas compounds (oxy-VOCs, terpenes, halogenated VOCs) and to clarify the overall measurement uncertainty needed in close collaboration with stakeholders (ACTRIS and WMO-GAW monitoring networks). In addition, to develop new primary RGMs at amount of substance fractions between 1 nmol/mol and 1 μ mol/mol (expanded uncertainty < 5 %) for oxy-VOCs and terpenes and < 1 nmol/mol (expanded uncertainty < 3 %) for halogenated VOCs (Objective 1)

Selection of priority VOCs relevant for climate in collaboration with stakeholders

Despite being present in the atmosphere at low amount-of-substance fractions, VOCs play an important role on the oxidising capacity of the atmosphere, climate and air quality. To protect the environment and minimise health risks from air pollution, VOC emissions and immissions are regulated by legislation (e.g. European Air Quality Directive 2008/50/EC). Thus, the amount-of-substance fractions of these compounds need to be monitored directly in the atmosphere. SI-traceable reference gas mixtures (RGMs) of target VOCs – with a low uncertainty but relatively long temporal stability – are necessary for reliable short- and long-term VOC measurements.

Because of the complex speciation of VOCs, with thousands of species, the first step to fulfil the first project objective was to elaborate a list of priority VOCs, in close collaboration with the stakeholder committee. METAS, VSL, LNE, PTB, Empa, IMTelecom, KIT, DWD and FMI elaborated an initial list of VOCs relevant for



atmospheric monitoring. The list was based on past work performed during the EMRP projects ENV56 HIGHGAS and ENV52 KEY-VOCs, on other research undertaken at an international level in the period 2015-2020 (e.g. other NMIs, universities, ACTRIS comparisons, etc.) and on end-user needs with respect to compliance with policies, regulation and instrument calibration. Information about compounds, amount fraction ranges and metrological requirements (i.e. traceability, uncertainty and stability) were extracted from literature, proceedings of meetings and workshops on atmospheric monitoring and previous project reports. METAS, VSL, LNE, PTB, Empa, IMTelecom and KIT sent this list to the project stakeholder committee, which included end-users and atmospheric modelling and remote sensing communities (e.g. ACTRIS, WMO-GAW, HITRAN). The final selection of priority VOCs was done based on their importance on climate research and the lack of stable and SI-traceable reference gas mixtures (RGMs) and included the required amount-of-substance fraction range, uncertainty and temporal stability.

The priority compounds considered are as follows:

- Oxy-VOCs: ethanol, methanol, acetone, acetaldehyde, methyl vinyl ketone (MVK), methacrolein
- Terpenes: α -pinene, β -pinene, myrcene, terpinolene, β -caryophyllene
- Halogenated VOCs: 1,2-dichloroethane, HFO-1336mzz-Z, HFC-134, HFC-124, desflurane

In consultation with a remote sensing group established during the project, which includes experts on satellite remote sensing, spectroscopic database and experimental cross-section, a list of relevant halogenated VOCs for remote sensing applications was elaborated. The halogenated VOCs selected were CF_4 (CFC-14), CF_2Cl_2 (CFC-12), CHF_3 (HFC-23), CH_2F_2 (HFC-32) and SF_6 .

Preparation of oxy-VOC RGMs at low amount-of-substance fractions and uncertainty

VSL and LNE prepared RGMs of priority oxy-VOCs at low amount-of-substance fractions following the gravimetric method described in ISO 6142-1:2015. VSL prepared 13 RGMs containing ethanol, methanol, acetone, acetaldehyde, MVK and methacrolein in nitrogen (BIP+, Air Products, quality better than 6.0) at 100 nmol/mol. Besides the priority oxy-VOCs, VSL added methyl ethyl ketone (MEK) and n-hexane, the latter as an internal standard to track the stability of the cylinder. Prior preparation, the purity of the liquid compounds was assessed by gas chromatography for organic impurities and the Karl Fischer titration method was used for water content. VSL also checked the quality of the nitrogen used: oxy-VOC traces ($\text{LoD} \leq 100 \text{ pmol/mol}$) were not found. LNE prepared 3 RGMs containing ethanol, methanol, acetone and n-hexane (internal standard) in nitrogen (BIP+) at 100 nmol/mol following the same method as VSL (ISO 6142-1:2015). LNE also assessed the purity of the liquid chemicals and matrix gas (nitrogen).

VSL and LNE started the RGM preparation with liquid injection of pure liquid chemicals in evacuated high pressure gas cylinders using nitrogen as the balance gas. The resulting binary gas mixtures of oxy-VOCs in nitrogen (50–100 $\mu\text{mol/mol}$) were diluted to lower amount-of-substance fraction mixtures in nitrogen. Depending on the amount fractions of the pre-mixtures and the targeted end-mixtures, sometimes, two or more steps of dilution were needed. VSL used four different types of cylinders for the filling of different material, volume and internal treatment, while LNE used two types.

VSL verified the prepared RGMs with dynamically generated gas mixtures in dry zero air in accordance with ISO 6145-8:2005 (diffusion method). For acetaldehyde, a continuous syringe injection method (ISO 6145-4:2004) and dynamic dilution in dry nitrogen (ISO 6145-7:2018) from higher amount-of-substance fraction mixtures using thermal mass-flow controllers were also applied. LNE performed the analytical verification by comparison with other RGMs dynamically diluted by means of a two-step dynamic dilutor (ISO 6145-7:2018). The mass flow controllers of the dilutor were coated to avoid surface effects. Furthermore, VSL and LNE assessed the temporal stability of the prepared RGMs during the 18 months (VSL) and 19 months (LNE) after preparation. VSL found a stable behaviour (well within their expanded uncertainty) for acetone, methacrolein and MEK. MVK seems to be slightly decreasing in time, but this loss needs to be further investigated. The behaviour of ethanol and methanol is cylinder dependent; in most cases, after initial loss, the observed amount-of-substance fractions of methanol and ethanol were stable or increasing to match the gravimetric values. The



best stability results were observed by cylinders with a specific internal treatment for oxy-VOCs and a low-dead volume cylinder valve. LNE found a stable trend for acetone and ethanol in both cylinder types. Although for the stainless steel coated cylinder, no significant methanol drift was found, a dramatic decrease of the methanol amount-of-substance fraction was observed in the other cylinder type (almost -50 % of the gravimetric value after 18 months).

According to VSL results, for the selected oxy-VOCs it is possible to prepare **RGMs in nitrogen at 100 nmol/mol** with an expanded **uncertainty** between **1.5 – 5 %** ($k = 2$) in agreement with the project objective. Typically, the expanded uncertainties for the specific compounds include uncertainty sources due to purity, gas mixture preparation and verification. Due to losses after preparation, VSL applied analytical values for methanol and ethanol instead of gravimetric values. In order to assess these losses, particularly for methanol, VSL developed a new methodology based on methanol isotopes. LNE prepared RGMs of acetone, ethanol and methanol at 100 nmol/mol. The uncertainty of the RGMs was $< 5 \%$ ($k = 2$), fulfilling the project target uncertainty, except for methanol ($U = 5.5 \%$) due to initial loss in one of the cylinder types (25 – 30 % loss). Combining VSL and LNE results, the preparation of new SI-traceable and stable (18 months) of oxy-VOC RGMs at low amount fractions (100 nmol/mol) and uncertainty ($\leq 5 \%$, $k = 2$) is possible for acetone, ethanol, methacrolein and MEK. For acetaldehyde, methanol and MVK, further research is needed. When preparing oxy-VOC RGMs selecting a good type of cylinder is crucial to ensure their stability.

In addition to the gravimetric RGMs prepared by VSL and LNE, METAS explored the suitability of dynamic methods based on permeation (ISO 6145-10:2002) for the generation of oxy-VOCs RGMs. Using one of METAS magnetic suspension balances (MSB) or one of the portable generators based on permeation, METAS generated RGMs of acetone, ethanol, methanol, methacrolein, MVK and acetaldehyde at different amount-of-substance fractions (5 – 100 nmol/mol). METAS calibrated the permeation units containing the pure liquid VOCs by placing each permeation unit in the MSB at different temperatures in order to estimate their permeation rate. METAS also assessed the purity level of the permeation units. After a stabilisation time dependent on the compound and the method used, METAS generated several RGMs. The generation by means of the METAS MSB showed that it is possible to generate **oxy-VOC RGMs at 10 – 50 nmol/mol in nitrogen** with expanded **uncertainties** between **0.7 – 3 %** ($k = 2$), except for ethanol ($U = 13 \%$, $k = 2$). In all cases, the main uncertainty sources were the estimated permeation rate and the impurities in the permeation units. The latter was particularly significant for the ethanol RGMs, contributing to $> 90 \%$ of the overall uncertainty. Ethanol permeation units with higher purity and longer calibration periods (2–3 weeks), could contribute to reduce the expanded uncertainty of the RGMs, potentially achieving the target expanded uncertainty. When using the portable generator, METAS found greater uncertainties (2 – 6 % and 16 % for ethanol, $k = 2$). The greater number of steps needed, which increases the number of uncertainty sources (e.g. long-term temporal stability of the permeation rate) and, thus, the overall uncertainty, explains the greater uncertainties.

In order to assess the newly developed RGMs, a comparison exercise was organised between LNE, METAS and VSL for oxygenated VOCs (oxy-VOCs) at 100 nmol/mol. Two sample gas mixtures, prepared respectively by LNE and VSL in cylinders, were used for the purpose and sent around for measurement. The main findings show that good comparability is demonstrated for acetone. For methanol, issues with initial loss/stability were observed in certain type of cylinders, however good agreement was found overall, especially considering that different RGM preparation methods (diffusion, permeation, dynamic dilution) were used for the measurements. These findings imply that dynamic methods are suitable for the generation of low amount fractions of polar oxy-VOCs. For ethanol, the interpretation of the results was more difficult, due to an analytical issue on the METAS results and a significant discrepancy between LNE and VSL for one of the two samples.

Preparation of terpene RGMs at low amount-of-substance fractions and uncertainty

METAS generated RGMs of selected terpenes, namely α -pinene, β -pinene, myrcene and β -caryophyllene at low amount-of-substance fractions (2 – 25 nmol/mol), using the dynamic method based on permeation (ISO 6145-10:2002). As for the dynamic oxy-VOC RGMs, METAS used a MSB and a portable generator based on permeation to generate terpene RGMs. METAS also calibrated and assessed the purity level of the permeation unit before the generation as described above. The expanded uncertainties ($k = 2$) of the α -pinene, β -pinene, myrcene and β -caryophyllene RGMs generated using a MSB were 7.1 %, 10 %, 13 % and 11 %, respectively. Expanded uncertainties of the terpene RGMs generated using the portable generator were 10 % for α -pinene and between 20 % and 25 % for the other compounds. None of the generated terpene RGMs showed an



expanded uncertainty close to, or lower than, the target one. In all cases, the main uncertainty source was the low purity levels of the permeation units (80 – 93.8 %) followed by the low long-term stability of the permeation range (contribution particularly important when using the portable generator based on permeation).

METAS' results show that the **permeation method** (as of mid-2022) is **not yet a suitable** method to generate **terpene RGMs** at very low amount-of-substance fractions (< 50 nmol/mol) and target uncertainties (< 5 %, $k = 2$). Further research, collaboration with manufacturers and the preparation of terpene RGMs using other methods (static and dynamic) might contribute to achieve project objective 1 for terpenes in the near future.

Preparation of halogenated RGMs at low amount-of-substance fractions and uncertainty

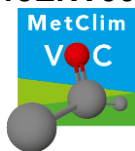
METAS prepared primary RGMs for 6 selected halogenated VOCs in synthetic air by means of the permeation method and subsequent cryo-filling into stainless steel cylinders coated with SilcoNert 2000 to achieve near ambient amount-of-substance fractions (low pmol/mol levels). METAS developed a cryo-filling system (improved version of the system developed during EMRP JRP ENV52 HIGHGAS), which precisely controls the mass flow, pressure and filling time. During the filling procedure, the cylinders were submerged in liquid nitrogen, making the gas condense in the cylinder (no pump required). A set of 8 cylinders (METAS 2021 scale) containing 3 halogenated VOCs from the priority list (1,2-dichloroethane, HFC-134, HFO-1366mzzZ) and 4 other halogenated VOCs (HFC-32, HFC-365mfc, CH_2Cl_2 , CCl_4) at near-ambient amount fraction (1.0-74.6 pmol/mol) was prepared using the cryo-filling system. The last four halogenated VOCs were selected because there are significant differences between the existing, non-SI-traceable scales. The halogenated VOCs 1,2-dichloroethane and HFO-1336mzzZ were included on the project priority list because there was no reference gas at atmospheric amount fractions available. The **RGM amount-of-substance fractions** were **< 1 nmol/mol** (from the lowest value of 1.0 pmol/mol for HFO-1336mzzZ up to the highest one of 74.6 pmol/mol for CCl_4) with an **expanded relative uncertainty** for all compounds **better than** the targeted 3 % ($k = 2$; 1.4 % for HFC-32, 2.3 % for HFC-365mfc, 1.7 % for dichloroethane, 0.8 % for carbon tetrachloride, 1.8 % for 1,2-dichloroethane and 2.1 % for HFO-1336mzzZ. Impurity checks of the carrier gas, the permeation devices and of the entire system were key to assess the uncertainty of the prepared halogenated VOCs, because the smallest impurity can have a huge influence in the pmol/mol range.

Summary

A list of priority oxygenated VOCs, terpenes and halogenated VOCs, which included information about the amount-of-substance fractions, temporal stability and expanded uncertainty needed to fulfil the data quality objectives of monitoring stations (e.g. WMO-GAW, ACTRIS), was prepared at the beginning of the project. This was done in close collaboration with stakeholders, achieving therefore the first part of objective 1. Furthermore, RGMs of priority oxygenated and halogenated VOCs were prepared within the target amount-of-substance fractions and expanded uncertainties (ca. 100 nmol/mol and $\leq 5\%$ ($k = 2$) and < 1 nmol/mol and < 3 % ($k = 2$), respectively). The objective was fulfilled for the oxy-VOCs acetone, ethanol, MEK and methacrolein, and for the halogenated VOCs: HFC-32, HFC-365mfc, dichloroethane, CCl_4 , 1,2-dichloroethane and HFO-1336mzzZ. The compounds for which the objective was not achieved and, thus, more research is needed were methanol, acetaldehyde and MVK (oxy-VOCs) and the priority terpenes (α -pinene, β -pinene, myrcene, terpinolene and β -caryophyllene).

4.2 To define and select fit-for-purpose protocols for the preparation of working standards that ensure an unbroken SI-traceable calibration chain for oxy-VOCs, terpenes and halogenated VOCs. In addition to validate these protocols (proof of concept) and to compare them with field calibration protocols as well as calculating the uncertainty budget for each protocol following the principles of GUM (ISO 1995) and taking into account other uncertainty sources on-site (e.g. water removal). To provide a homogenous tool for uncertainty calculation for end-users (Objective 2).

Development of protocols for preparing SI-traceable working standards



IMTelecom, in collaboration with FMI, KIT, Empa, DWD and METAS, elaborated a report summarising the existing VOC calibration strategies that are currently applied to the Gas Chromatography-Flame Ionization Detector (GC-FID), Gas Chromatography-Mass Spectrometry (GC-MS) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS) instruments that are used at European measurement sites for VOC monitoring. The report described the most common calibration strategies for GC-FID and GC-MS, which are the direct use of SI-traceable RGMs in cylinders, the effective carbon number, the dilution of higher amount fraction RGMs and permeation tubes. In the case of terpenes, the dilution of pure compounds (liquid form) in methanol and its preconcentration on adsorption tubes is also a common strategy. PTR-MS calibration strategies followed the use of non-SI-traceable gas standards or, alternatively, the ion transmission curve. Currently, SI-traceable transmission curve reference material developed by NPL for PTR-MS is available (<https://doi.org/10.5194/amt-16-1061-2023>).

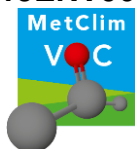
The report highlighted the extended **use of non-SI-traceable approaches to calibrate** the instruments at monitoring stations measuring VOCs. The project, thus, targeted the **gaps in SI-traceability** in order to develop fit-for-purpose SI-traceable working standards. For that purpose, METAS, Empa, VSL, IMTelecom, UU and POLITO, with support from LNE, DWD and FMI, elaborated protocols for the propagation of RGMs to working standards with an unbroken SI-based traceability chain for oxy-VOCs, terpenes and halogenated VOCs. In these protocols, new working standards developed during the project such as the gravimetric RGMs mentioned above (100 nmol/mol, U < 5 %) diluted to atmospheric levels using a SI-traceable dilution system or certified whole air working standards, were described.

Four different approaches were contemplated to develop the protocols for oxy-VOC SI-traceable working standards by METAS, VSL, Empa, IMTelecom, POLITO and UU, in collaboration with LNE, DWD and FMI. The first approach consisted of the dynamic dilution of the oxy-VOC RGMs prepared by VSL to fulfil the objective 1 of the project. Two different dilution systems were considered: VSL dilution system and METAS dilution system (VerDi), which was developed during the project to provide a portable SI-traceable dilution system. Two different cylinders of VSL RGMs were sent to IMTelecom, Empa and UU to perform the assessment of the new SI-traceable working standards, together with the detailed protocol to prepare this type of working standard. The second approach was based on permeation and consisted of the use of METAS portable generator and calibrated permeation units of the selected VOCs under study. The calibration of the permeation units was done by METAS. The third approach was based on the diffusion method and consisted of the use of VSL and POLITO's in-house diffusion systems. The final approach consisted of working standard protocols based on spiked and certified whole air samples. The air samples were collected by Empa, the spiking was done by METAS and the certification of oxy-VOCs was performed by VSL and METAS.

For terpenes, METAS and Empa developed two protocols based on two of the approaches described for oxy-VOCs: the approach based on permeation and the one based on spiked and certified whole air samples. Empa and METAS also developed the protocol to prepare SI-traceable working standards of halogenated VOCs. This protocol was based on the preparation of SI-traceable RGMs (the ones described in objective 1) and their subsequent intercomparison with real-air standards.

Assessment of the developed protocols by comparison with field calibration protocols

The novel SI-traceable working standards were compared against the current standards used at monitoring stations to assess the best practice protocol for working standards. For the assessment of the protocol describing the preparation of SI-working standards based on whole air, several steps were done. First, whole air samples were collected at Rigi Mountain (Switzerland) and filled into high-pressure cylinders and low-pressure canisters by Empa (a total of 30 samples). The next step of the assessment was to certify the samples – previously spiked with the priority oxy-VOCs and terpenes at METAS – by VSL and METAS. For this purpose, two batches were sent to both institutes, who had two samples in common (a kind of transfer standard). Certification was only possible in the high-pressure cylinder for methanol, ethanol, acetone and methacrolein. For the 10-L aluminium cylinders, the certified values were (12.8 ± 2.0) nmol/mol, (11.2 ± 2.6) nmol/mol, (17.0 ± 1.5) nmol/mol and (10.7 ± 1.0) nmol/mol, respectively. For the samples stored in the 3.6 L stainless steel SilcoNert 2000 coated cylinders the certified values were (9.8 ± 2.5) nmol/mol, (7.6 ± 1.9) nmol/mol, (17.3 ± 1.1) nmol/mol and (10.2 ± 0.9) nmol/mol, respectively. Certified values were possible only for methacrolein and acetone in the low-pressure canisters: (17.2 ± 3.7) nmol/mol and (13.3 ± 2.6) nmol/mol respectively in 15 L Silonite canisters and (13.4 ± 2.9) nmol/mol and (8.3 ± 1.2) nmol/mol in the 6 L canisters.



After the certification, another 3 batches of cylinders and canisters was sent to UU, DWD and IMTelecom by Empa, to perform a round-robin comparison. The three participants got the same high-pressure cylinders, which were analysed at different periods. A fourth batch was kept at Empa to assess its temporal stability. Participants used different analytical instruments and calibration protocols (Table 1) to measure the oxy-VOC amount-of-substance amount fractions in the air samples.

Table 1: Analytical instruments and calibration protocols used by the partners participating in the round-robin comparison of spiked whole air samples.

Partner	VOC category	Assessment dates	Analyser	Calibration (in-house) working standard
Empa*	oxy-VOCs	Aug. 2021, Nov. 2021, May 2022, Aug. 2022, Nov. 2022	GC-FID	NPL NMHC standard + carbon number
DWD	terpenes	Mar. 2022	GC-FID	NPL-1 ppb standard
DWD	terpenes	Mar. 2022	GC-FID	NPL-12 VOC standard
IMTelecom	oxy-VOCs	Jun.-Jul. 2022	PTR-MS	NPL PTR-MS standard
IMTelecom	terpenes	Jun.-Jul. 2022	GC-FID	NPL 4 ppb NMHC standard
UU	oxy-VOCs	Sep. 2022	PTR-MS	NPL PTR-MS standard
VSL**	oxy-VOCs	Jul.-Aug. 2022	GC-FID	Diffusion method
METAS**	oxy-VOCs	Feb. 2022	GC-FID	Portable generator based on permeation
METAS**	terpenes	Feb. 2022	GC-FID	Portable generator based on permeation

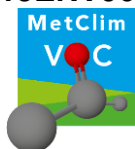
*Temporal stability assessment; **Certification

The results were quite diverse. Whereas high-pressure cylinders seem to be suitable for the less polar oxy-VOCs (acetone and acetaldehyde) for up to 12 months, the low-pressure canisters should not be used for these compounds. For more polar compounds, such as methanol and ethanol, this kind of working standard is not suitable. Terpenes showed an initial loss in both types of vessels (high-pressure cylinders and low-pressure canisters). For myrcene and β -caryophyllene, peaks were not observed neither during the certification nor during the comparison, although both compounds were spiked into the vessels. For α -pinene and β -pinene, peaks were observed but with an uneven behaviour. It was concluded, therefore that whole air samples should not be considered as working standards for terpene monitoring.

In addition to the whole air samples, another 4 protocols were assessed against field/in-house working standards by VSL, IMTelecom, Empa, UU and POLITO, which used several analytical instruments (2 PTR-MS, 5 GC-FID and 1 analyser based on laser spectroscopy) and different calibration protocols (Table 2).

Table 2: Analytical instruments and calibration protocols used by the partners participating in the assessment of SI-traceable working standards.

Partner	VOC category	New SI-traceable working standard	Assessment dates	Analyser	Calibration (in-house) working standard
VSL	oxy-VOCs	VSL RGM + VSL dilution system	Aug. 2022	GC-FID	Diffusion
IMTelecom	oxy-VOCs	VSL RGM + METAS dilution system	Jun. 2022	PTR-MS	NPL PTR-MS standard
IMTelecom	oxy-VOCs	Portable generator + calibrated permeation units	Jun. 2022	PTR-MS	NPL PTR-MS standard

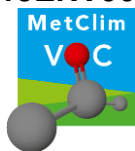


Partner	VOC category	New SI-traceable working standard	Assessment dates	Analyser	Calibration (in-house) working standard
IMTelecom	terpenes	Portable generator + calibrated permeation units	Jul. 2022	GC-FID	NPL 4 ppb NMHC standard
DWD	terpenes	Portable generator + calibrated permeation units	Mar. 2022	GC-FID	NPL-12 VOC standard
DWD	terpenes	Portable generator + calibrated permeation units	Mar. 2022	GC-FID	NPL 1 ppb standard
Empa	oxy-VOCs	VSL RGM + METAS dilution system	Nov. 2022	GC-FID	NPL NMHC standard + carbon number
Empa	oxy-VOCs	Portable generator + calibrated permeation units	Nov. 2022	GC-FID	NPL NMHC standard + carbon number
UU	oxy-VOCs	VSL RGM + METAS dilution system	Sep. 2022	PTR-MS	NPL PTR-MS standard
POLITO	oxy-VOCs	POLITO diffusion system	Mar. 2023	GC-FID	RGM + dynamic dilution
POLITO	oxy-VOCs	POLITO diffusion system	Mar. 2023	Laser spectroscopy analyser	RGM + dynamic dilution

VSL, IMTelecom, DWD, Empa, UU and POLITO calculated the VOC measured amount-of-substance fractions in the samples, while METAS estimated the theoretical amount-of-substance fractions of the new SI-traceable working standard. Relative differences between measured and theoretical VOC amount-of-substance fractions were calculated, as well as the uncertainty of the difference to evaluate the agreement between the pair of values. Results suggest that the new SI-traceable working standard protocols seem to be suitable for acetone monitoring but not for MVK, MEK or methanol. Although SI-working standards based on diluted reference gas mixtures seem to be suitable for acetaldehyde, SI-working standards based on permeation are not. For methanol, clear conclusions could not be extracted, but it seems that it remains a challenging compound. Because of the broad variety of instruments and calibration standards, the conclusions should be taken with caution. SI-traceable working standards based on a permeation seem to be unsuitable for terpene monitoring, particularly for α - and β -pinene. This was due, most likely, to the low long-term stability and purity of the permeation units. Alternatives to SI-WS based on permeation, such as dilution of reference gas mixtures using SI-traceable dilution systems should be explored.

User friendly on-line uncertainty calculation tool for VOC measurements – TUCAVOC

METAS, IMTelecom, Empa and POLITO identified the main sources of uncertainties of each analytical technique and calculated the uncertainty budgets of each measurement method considering all the processes involved in the measurement: sampling, calibration and analysis. For each of the analytical methods used during the working standard assessment, the main sources of uncertainty were identified, described and quantified. Based on the project outputs for GC-FID, as well as on the guidelines described by ACTRIS and WMO-GAW regarding the uncertainty of this technique for VOCs, an on-line tool for the calculation of uncertainties (TUCAVOC) was developed and made available for monitoring stations. The first version of the on-line tool is currently under review and improvement process based on the implementation of comments provided by NMIs and monitoring station operators. Documentation and executable files are freely available under: <https://tucavoc.readthedocs.io/en/latest/about.html>.



Summary

During the project, protocols for the generation of SI-traceable working standards were defined for oxy-VOCs (4 protocols), terpenes (2 protocols) and halogenated VOCs (1 protocol). These protocols were based on different methods such as dilution of RGMs at high amount-of-substance fraction, permeation, diffusion and spiked and certified ambient air. Once the protocols were developed, they were validated in a complex comparison exercise, where the new working standards were compared to routine ones. The new working standards, especially the ones based on RGM dilution, seems to be appropriate for all oxy-VOCs except for methanol, MVK and MEK. For terpenes, further research to define suitable SI-traceable working standards is needed. The uncertainty budget of each working standard (non-traceable and SI-traceable) was calculated by the consortium. To fully achieve objective 2, an on-line tool to calculate the uncertainty of measurements in a user-friendly way was developed and distributed among the atmospheric monitoring community.

4.3 To evaluate the sampling methods for the on-line/off-line in-situ analytical measurement of the selected gas compounds and to assess relevant influence parameters. In addition, to evaluate and improve the on-line/off-line in-situ analytical methods. To determine spectral molecular parameters for spectroscopic techniques, used in remote sensing methods to assess VOCs, with SI-traceability and contribute these to the HITRAN database. To establish an uncertainty budget for the selected measurement methods (Objective 3).

Evaluation of sampling methods

Several tests were performed to evaluate the sampling methods used for the analytical measurement of the priority VOCs (oxy-VOCs, terpenes and halogenated VOCs). Protocols for testing sampling lines, particle filters, water removal systems and ozone scrubbers, which are commonly part of the VOC sampling strategy, were defined and tested by IMTelecom, POLITO, UU, FMI, Empa and DWD. Moreover, FMI and TUBITAK evaluated different sorbent materials to assess the suitability of the tested sorbent tubes as an off-line method for measuring oxy-VOCs and terpenes.

1. Sampling lines

Results obtained by IMTelecom and UU and analysed in collaboration with POLITO showed that, at relative humidity (RH) between 30-70 %, the tested sampling line materials (Silcosteel, Sulfinert, stainless steel, PFA and PEEK) did not have important effects on the sampled oxy-VOCs (relative difference = ± 4 %), which are typical examples of the more volatile group (methanol, acetaldehyde, acetone and MVK) as well as the group of hydrocarbons (toluene). However, under dry conditions (not typical of ambient measurements) IMTelecom, UU and POLITO observed effects regarding the response time of different compounds. For instance, higher molecular weight oxy-VOCs showed a longer delay, which was more pronounced when measured under dry conditions. These effects can be minimised by using passivated sampling lines. Sampling lines, especially polymers, should be passivated for several days before ambient air measurements to eliminate any traces of compounds remaining in the lines.

FMI found that FEP, Silcosteel-CR and Sulfinert inlet lines (internal diameter 1/8", length 10 m) are suitable for measurements of the priority compounds of the project using a sampling air flow of 1 L/min under both dry and wet conditions (30 % and 70 % RH, respectively). PEEK inlet, however, is not recommended for terpenes as losses of the priority terpenes and terpinolene were observed.

2. Particle filters

IMTelecom evaluated potential effects of three different types of particle filters (PTFE, stainless steel and Balston) on oxy-VOC and terpene amount-of-substance fractions. The particle filters were new and used. IMTelecom found that the use of a new particle filter can slightly affect the measured amount-of-substance fractions of oxy-VOCs (relative difference = ± 5 %), while used particle filters had a more significant effect (relative difference = $\pm 6 - 10$ %). IMTelecom found similar results for α -pinene and β -pinene (relative difference = ± 2 %). Effects on limonene amount-of-substance fractions were greater than for the other two terpenes (relative difference ± 2 %) when using new filters. IMTelecom observed, as expected, that placing used filters in the sampling system can lead to the loss and/or emissions of compounds of up to 10–15 %.



Thus, during field campaigns, it is recommended to change particle filters every 5-7 days depending on the concentration of particles on the ambient air, as well as on VOC amount-of-substance fractions.

3. Water removal systems

Empa and IMTelecom evaluated two types of water removal systems (cold finger, Nafion Dryers). For the cold finger system, IMTelecom results showed the efficient capacity (> 90 %) of the cold finger to remove significant amounts-of-substance fraction of water when it is used at low temperatures (-40 °C and -30 °C). However, the efficiency decreases to 88.9 % when the temperature of the water trap is set to -10 °C. Cold finger can affect some of the priority oxy-VOCs leading to losses up to 20 % (e.g. MVK). This effect seems to be less important as the temperature of the water trap increases to -10 °C. However, taking into account the low efficiency of the water removal at that temperature, -30 °C is the recommended operated temperature. Complete loss of the more polar oxy-VOCs occurred when Nafion Dryers were used. Empa results on the selected water removal systems (cold finger, Nafion Dryers) suggest that none of them might have effects on the amount-of-substance fraction measured for halogenated VOCs (CFCs, HCFCs, HFCs, PFCs, HFOs). Attention should be given to the type of water removal system used and its parameters when sampling particularly oxy-VOCs at ambient amount-of-substance fractions.

4. Ozone scrubbers

IMTelecom, DWD, FMI and Empa tested four different types of new and used ozone scrubbers (KI/Cu, MnO₂, Na₂S₂O₃ and heated stainless steel tubes). Both ozone removal efficiency and potential effects on the amount-of-substance fractions of oxy-VOC, terpene and halogenated VOC targeted compounds were evaluated. The majority of the ozone scrubbers showed an efficiency greater than 95 %, except Na₂S₂O₃ ozone scrubber that had an efficiency between 60–70 %. The lower efficiency might be linked to a higher air flow (800 mL/min) than common field flow values (80 mL/min) passing through the ozone scrubber, resulting in a smaller residence time and, thus, lower efficiency. According to IMTelecom and Empa results, the use of a KI/Cu, MnO₂ and Na₂S₂O₃ ozone scrubber during sampling does not affect the measured oxy-VOC or halogenated VOC amount-of-substance fractions by more than 3.5 % for halogenated VOCs and most of the oxy-VOCs, except for methanol, for which larger effects were observed (~10 %). Also for the stainless steel trap losses of about 5 % were observed when ozone was added. DWD results for terpenes under dry conditions showed losses for at least some of the terpenes for almost all the traps. Best performer under dry conditions was the Na₂S₂O₃ ozone trap only showing losses of myrcene, the sum of ocimene-limonene-123trimethylbenzene and 3-carene. Largest losses are observed for the used KI/Cu trap for compounds >C₈. In addition, DWD checked possible artefacts and memory effects during these experiments. Some memory effects observed for KI/Cu under dry conditions. For the Na₂S₂O₃ trap a memory effect is observed for eucalyptol and camphor, while for heated SS trap only some residual camphor is observed. Under wet conditions all scrubbers perform well without losses, and no additional peaks have been observed in the MS spectra. Thus, DWD recommends to apply O₃ traps upstream of the water traps in an analytical system. FMI's results on O₃ traps indicated that Na₂S₂O₃ filters, heated SS tubes and KI/Cu-traps are suitable for the measurements of target terpenes while terpinolene and β-caryophyllene as well as most other studied sesquiterpenes and some monoterpenoids had significant losses in MnO₂ traps. In addition, KI/Cu-traps may have losses of some sesquiterpenes (β-farnesene) other than the target one (β-caryophyllene). It should also be noted that the flow used for the KI/Cu-traps was clearly higher (1 L/min) than for the other traps (0.08-0.1 L/min) and with the lower flow KI/Cu-traps may have more losses. Summarising, the use of KI/Cu, MnO₂ and Na₂S₂O₃ ozone scrubbers does not have effects on the sampled oxy-VOCs and halogenated VOCs. For terpenes, the tested ozone scrubbers are suitable except MnO₂, which showed effects on the sampling of mono- and sesquiterpenes.

5. Sorbent tubes for off-line VOC measurements

In order to improve the off-line methods used for measuring oxy-VOCs and terpenes, FMI and TUBITAK ran different tests to evaluate sorbent tubes for oxy-VOC and terpene sampling. TUBITAK's results showed that of the 9 tested materials Carbpac, C-Carbpac, B-Carbsieve SIII, and Carbsieve SIII were the most suitable sorbent materials for the target oxy-VOCs, except for methanol. Tested oxy-VOCs were found to be stable in Carbpac, C-Carbpac, B-Carbsieve SIII, and Carbsieve SIII tubes when stored for 1 month at -20 °C while with storage temperature +20 °C some deviations were observed. Very low breakthrough volumes were observed for most of the target oxy-VOCs. Methanol was not retained quantitatively even with a 0.1 L sampling volume. For acetaldehyde, acetone, ethanol no breakthrough was



observed with 0.1 L and for methacrolein and MVK the breakthrough volume was at least 1.0 L. For terpenes, FMI results showed that Tenax TA in stainless steel or Silcosteel tubes was most suitable, while with Carboxpack B significant losses of β -pinene, terpinolene and β -caryophyllene were observed. Based on the earlier literature and results from this study, target terpenes were found to be stable in Tenax TA tubes for at least one month at ± 20 °C. Conducted breakthrough tests indicated that α - and β -pinene have clearly lower safe sampling volumes in Tenax TA (4-7 and 8-26 L, respectively) than other terpenes (>160 L) and breakthrough volumes in Carboxpack B tubes are very high (>160 L) for all studied terpenes. In Carboxpack B tubes, β -pinene, terpinolene and β -caryophyllene had severe losses. At the same time, the concentration of some terpenes (i.e., camphene) increased. This indicates that some terpenes can be isomerised forming other terpenes in the Carboxpack B tubes. Summarising, FMI and TUBITAK's results showed that the best sorbent material for sampling terpenes (α -pinene, β -pinene, myrcene, terpinolene and β -caryophyllene) is Tenax TA (commercial), while for oxy-VOCs (acetaldehyde, methanol, acetone, ethanol, methacrolein and methyl vinyl ketone) it is Carboxpack C – Carboxpack B – Carboxsieve SIII and Carboxsieve SIII (commercial). The differences between stainless steel and coated Silco steel tubes were not significant.

Development and evaluation of analytical methods

IMTelecom, in collaboration with IL, TUBITAK, KIT, Empa, DWD and METAS, made an inventory of existing analytical methods for oxy-VOCs and terpenes early in the project. The inventory describes existing techniques used to measure the targeted VOCs in ambient air and includes a subsection focusing on techniques and difficulties of measuring formaldehyde. The techniques developed and evaluated during the project were selected based on the main findings of the inventory.

1. Side by side comparison of techniques for measuring formaldehyde

IMTelecom organised and participated in a formaldehyde side by side comparison. Together with other participants, external to the project, six different techniques to monitor formaldehyde were evaluated: three instruments based on Hantzsch fluorimetry, one instrument based on microfluidics Hantzsch fluorimetry, two DNPH samplers, one analyser based on IR spectroscopy, a PTR-MS and one instrument based on CRDS. Different levels of formaldehyde were generated, using either a gas cylinder or a permeation system (Permacal) with a formaldehyde permeator. Both, the gas cylinder and formaldehyde calibration unit were certified by VSL and METAS, respectively. According to the comparison results, the DNPH as a reference technique performed very well compared to theoretical generation. Moreover, the CRDS-based instrument is the least noisy method to measure formaldehyde at low amount fractions (≤ 5 nmol/mol) followed by the 3 Hantzsch-based instruments and microfluidics. The great majority of the instruments succeeded to measure all the different levels of formaldehyde apart from the IR-spectrometry-based instrument, which was noisy. A fast response when changing the formaldehyde amount-of-substance fractions was observed for all the instruments except the microfluidics Hantzsch fluorimetry. Subsequently, compared to the DNPH measurements (reference technique), the CRDS-based instrument showed differences 1-3 % for the generation experiments, while the three Hantzsch-fluorimetry-based instruments showed positive differences from 1-11 %. Moreover, the IR-spectrometry-based instrument did not succeed in measuring amount fractions below 5 nmol/mol but over this threshold it underestimated the amount fractions by 9-12 % during the first three days of generation, and 60 % during the last day, which could be partially explained by a potential trapping of formaldehyde onto the particle filter droplets. The PTR-MS instrument overestimated the amount-of-substance fractions by about 40-80 %, which reflects clearly that the instrument is not suitable for measuring formaldehyde at such low amount fractions most likely due to calibration and corrective actions that should be performed. Finally, the microF is also able to quantify the formaldehyde amount fractions down to few nmol/mol with differences within 13 %, when considering the corrected data. Taking into account all these results, it should be noted that DNPH, Hantzsch-fluorimetry-based instruments and CRDS-based instruments are more robust for measuring formaldehyde at extremely low amount fractions. Taking into account the DNPH correction, microF showed good results but with potentially higher uncertainty due to the problem in performing a post-calibration. The IR-spectrometry-based instrument, however, is not suitable for measuring low amount fractions since this version of the instrument is dedicated to indoor air quality measurements at higher amount fractions. In addition, the PTR-MS technique is not made for measuring this compound due to limitations on the principle



itself as it was confirmed during this intercomparison. Finally, it should be noted as well that there are possible artefacts of $\pm 4-7\%$ of HCHO under typical ozone conditions, which are considered to be inside uncertainties (i.e., relative uncertainty of theoretical values = 5.6 %), thus the ozone impact can be considered negligible. To sum up, this interlaboratory comparison pointed out the necessity to have an SI-traceable calibration standard for a sticky compound such as formaldehyde and the need to perform QA/QC measures, especially to address interferences. The laboratory platform is optimised for such exercises and it works well. The formaldehyde generation with the two tested different generation methods showed stable results

2. Optimisation of a new methanol analyser based on laser spectroscopy

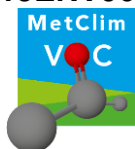
As a result of a collaboration between POLITO and the instrument manufacturer GASERA, a fit-for-purpose methanol analyser was developed and characterised. The analyser was customised for continuous fast (0.1 Hz) measurements of methanol in gas at low amount-of-substance fractions. Although the analyser is optimised for measuring methanol, other VOCs and limits of detection can be measured by modifying the light source and modifying properly the data analysis software. The sample flow is approximately 800 mL/min in a standard configuration given by the vacuum pump at the exit of the system. POLITO performed different tests in the laboratory to evaluate and optimise the methanol analyser. Based on this characterisation, some considerations should be taken into account to ensure the quality of the measurements with the GASERA ONE Methanol analyser, such as providing humidity to the instruments, as it helps to passivate the sampling lines. At amount-of-substance fractions above 1000 nmol/mol of methanol, the measurement parameters started to have a significant impact on the values obtained due to transient effects inside the instrument associated to wall interactions. In general, the variability of readings after stabilisation was improved significantly when the number of cell flush cycles increased in order of magnitude, even with the same short default duration of flush through cell and bypass. At high levels of methanol, after fast switches, a minimum time of 5 minutes is required for the system to stabilise to a new value. Furthermore, using sampling lines of passivated material (i.e. Sulfinert or Silcosteel) it is recommended to minimise wall interactions, as well as performing the stabilisation of the lines by passing a humid gas mixture through the system for 24 hours prior to the measurements.

3. A SI-traceable PTR-MS standard

A new SI-traceable PTR-MS standard developed by NPL (<https://doi.org/10.5194/amt-16-1061-2023>) was tested by UU using three different PTR-MS instruments. The standard, containing 20 relevant compounds at the same amount fraction (1 $\mu\text{mol/mol}$) covers a wide mass range. Based on the developed transmission curve reference material, UU drafted a protocol for retrieving the transmission parameter of the instrument, assessing the slope of local transmission, assessing primary ion purity, collision energetics, humidity in the reaction chamber and water cluster ions.

Validation of spectral parameters

PTB conducted accurate measurements of CF_4 , SF_6 and CHF_3 . Pressure and temperature measurements were fully traceable. PTB used a dynamic dilution system allowing significantly better control over the absorber's amount-of-substance fractions than the conventional mixing method. For room temperature, PTB, with the advice of UoL, applied a technique to reconstruct the absorption cross sections over a large span of amplitudes. This resulted in two spectra for CF_4 and SF_6 each and one spectrum for CHF_3 . Generation of the composite spectra proved to be very accurate and straightforward for the non-polar molecules. In the case of the CHF_3 molecule, which has a dipole moment, attention should be (and has been) paid to the possible effect of collisions between the absorber molecules, which can affect the absorption profile. Analysis of the integrated intensities yielded accurate values with uncertainties below 1.8 % ($k = 2$), with the absorption path being the major contributor. PTB results validate the data from the PNNL database for the CF_4 molecule, but also point out a desirable correction of the data for SF_6 by about 2 %. There is an excellent agreement for the major fundamentals of CHF_3 , but the low wavenumber ν_3 band from PNNL is 2 % smaller than ours. Excellent data by UoL, available for a broad interval of temperatures, can be re-adjusted to a more precise value using these updated integrated intensities. Maintainers of the HITRAN database have been notified about the current study. The overall uncertainties obtained by PTB fulfill the current needs of the remote sensing community.



Uncertainty budget of the selected methods

IMTelecom, Empa and POLITO, in collaboration with METAS, selected three analytical methods commonly used to measure oxy-VOCs, terpenes and halogenated VOCs and a novel method to analyse methanol. The selected methods were Proton Transfer Reaction-Mass Spectrometry (PTR-MS), Thermal Desorption-Gas Chromatography-Flame Ionization Detection (TD-GC-FID), Medusa-GC-MS and an analyser based on laser spectroscopy, respectively. For each method, IMTelecom, Empa and POLITO provided measurement guidelines with recommendations on the set-up, operating conditions, procedures of calibration, sampling and analysis, as well as on the data processing and quality checks. The recommendations were based on the results obtained during the evaluation of sampling and analytical methods. Then, IMTelecom, Empa and POLITO with the guidance of METAS, specified the measurand for each method (i.e. amount-of-substance fraction), formulated the equations required to estimate the values, identified the uncertainty sources and quantified the uncertainties and report this information, taking an example of measurement for each method, in the calculated uncertainty budgets. The uncertainty budgets were simplified whenever it was possible to do it.

1. Uncertainty budget of PTR-MS measurements of oxy-VOCs

IMTelecom identified as the main sources of uncertainty the uncertainties of the calibration standard, which included the uncertainty of the preparation and the stability of the calibration standard, the uncertainty due to the instrumental precision of the measured sample, the uncertainty coming from the use of any element for sampling (such as sampling lines, particle filters and ozone scrubbers) and the uncertainty of the measurements performed close to the limit of detection (LOD). IMTelecom calculated the combined uncertainty by applying the square root to the sum of squares of the standard uncertainties of each of the described uncertainty sources. By multiplying the result by two, IMTelecom calculated the expanded uncertainty of the oxy-VOC amount-of-substance fraction.

2. Uncertainty budget of TD-GC-FID measurements of terpenes

IMTelecom defined the main uncertainty sources contributing to the overall uncertainty of the terpene measurements performed using TD-GC-FID. For that purpose, IMTelecom referred to the guidelines established by ACTRIS to estimate the overall uncertainty of TD-GC-FID measurements (also considered by Empa for developing the on-line tool TUCAVOC). The main sources of uncertainty were the uncertainty of the calibration standard (u_{cal}), the uncertainty associated to the reproducibility of the measurement method (u_{prec}), the uncertainty of the analytical method (u_{an}) mainly due to integration errors (u_{int}), lack of linearity (u_{lin}) and instrumental problems such as artefacts, changes of split flow rates (u_{instr}). Other sources to be considered are the uncertainties due to measurements close to the limit of detection of the instrument (u_{LOD}), which is included in the uncertainty of the method reproducibility, and uncertainties associated to off-line sampling methods (u_{offsm}) such as sorbent tubes (e.g. storage issues, sampling volume accuracy...). IMTelecom calculated the combined uncertainty of the measurement as follows:

$$u_c(x_{VOC}) = \sqrt{u_{cal}^2 + u_{prec}^2 + u_{int}^2 + u_{lin}^2 + u_{instr}^2 + u_{sm}^2}$$

By multiplying by a coverage factor of 2, IMTelecom calculated the expanded uncertainty of the measurement. This expanded uncertainty was calculated assuming that the measured terpenes were present in the calibration gas mixture and, therefore, the amount-of-substance fractions were certified by the gas supplier. When the amount-of-substance of calibration standards and samples are greater than the instrument LOD, u_{LOD} can be discarded.

Table 3: Example uncertainty budget of a measured terpene using a TD-GC-FID. The terpene estimated amount fraction in the sampled air was 14.8 nmol/mol.

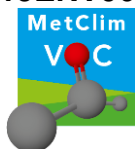
Quantities/ Uncertainty sources	Value [x _i]	Unit	Unc. type	Probability distribution	Divisor	Standard uncertainty [u(x _i)] (nmol/mol)	Significance check (%)
Sampling							



Quantities/ Uncertainty sources	Value [x _i]	Unit	Unc. type	Probability distribution	Divisor	Standard uncertainty [u(x _i)] (nmol/mol)	Significance check (%)
sampling volume	0.6	L	B	uniform	√3	negligible	
u _{smp} [k = 1]						negligible	
Calibration							
X _{RGM}	100	nmol/mol	B	normal	2	2.5	49.8
u _{cal} [k = 1]						2.5	-
Analysis							
Reproducibility	14.5	nmol/mol	A	normal	2	0.16	3.2
Limit of Detection (LOD)	0.007	nmol/mol	B	normal	2	negligible	
Sample peak integration	21201	area units	A	normal	2	992 (area units)	-
Calibration peak integration	55807	area units	A	normal	2	876 (area units)	-
u _{int} [k = 1]						0.08	1.6
Instrument linearity	-	nmol/mol	A	normal	2	negligible	
Instrumental problems (e.g. artefacts)	-	nmol/mol	B	uniform	√3	negligible	
u _{an} [k = 1]						0.18	-
						nmol/mol	relative (%)
Combined uncertainty u _c (y) [k = 1]						2.51	17.0 %
Expanded uncertainty U [k = 2]						5.02	34.0 %

3. Uncertainty budget of laser spectroscopy measurements of methanol

For the commercial analyser, GASERA (project collaborator) implemented the necessary mathematical models in the instrument software to estimate the uncertainty of the measurements. GASERA also provides a certificate of calibration of each methanol analyser. Several quantities are controlled during the default operation of the analyser as a means of minimising their influence on the total uncertainty of the measurement. POLITO found during the optimisation tests for this analyser that the humidity level of the sample plays an important role in the accuracy and stability of the measurements. If the influence quantities represent relevant sources of uncertainty (i.e. accounting for over 10 % of the total uncertainty), these quantities should be included in the uncertainty budget. POLITO estimated the sensitivity coefficient from polynomial regression over the experimental results. The sampling system handling the gas upstream of the analyser should be evaluated for uncertainty as well. The quantities associated to the sampling system are mostly related to losses due to surface interactions. The uncertainty associated to interaction depends not only on the substance but the humidity and the wall material. POLITO used results from the experimental tests to estimate the expected rate of interaction due to sampling lines to be included in the evaluation of the uncertainty. The expanded uncertainty reported by GASERA in the calibration certificate



of the analyser, includes the following uncertainty sources: influence of the limit of detection, linearity and drift, and the uncertainty of the calculated amount of fraction from the spectra and of the RGM used for calibration. To that value, the sampling contribution as the rate of mass loss can be added in case is not negligible. However, for atmospheric measurements of methanol (sub 10 nmol/mol), a tubing length of up to 15 m (1/4") provides negligible losses due to interactions. When performing calibration with a GASERA analyser, the uncertainty of the instrument is added to that of the RGM used during the calibration and if needed, the expected contribution of mass loss due to sampling devices.

$$u(x) = \sqrt{u^2(x_{\text{RGM}}) + u^2(x_{\text{internal}}) + u^2(x_{\text{sampling}})}$$

POLITO estimated the uncertainty of the generated gas mixture as a combined uncertainty based on the Type A uncertainty of repeated measurements performed on different days, under the same conditions of temperature and the Type B uncertainty of the certificate of the CGM. For that purpose, MFM values of the dilution air and mixture flows were used. This estimation was performed to verify the stability of the generated mixture, which for the case study resulted in a standard uncertainty of 0.05 nmol/mol (as reproducibility from the pooled standard deviation during 3 independent runs of 10 min). The mixing device has limited area and is entirely made of Sulfinert®, ensuring negligible wall interaction, for which this parameter was not included in the equation/uncertainty budget. POLITO estimated the theoretical amount-of-substance fraction used as methanol mixture during the experiments as follows:

$$x_{\text{theo}} = \frac{q_{v_{\text{mix}}} \cdot q_{vs_{\text{mix}}} \cdot x_{\text{mix}}}{(q_{v_{\text{air}}} \cdot q_{vs_{\text{air}}} + q_{v_{\text{mix}}} \cdot q_{vs_{\text{mix}}})}$$

where,

x_{theo} : theoretical amount fraction of the measured mixture (in nmol/mol)

$q_{v_{\text{mix}}}$: flow rate of the gas mixture (in %)

$q_{v_{\text{air}}}$: flow rate of the dilution gas (in %)

$q_{vs_{\text{mix}}}$: flow range of the MFM measuring the flow of the mixture (in mL/min)

$q_{vs_{\text{air}}}$: flow range of the MFM measuring the flow of the dilution gas (in mL/min)

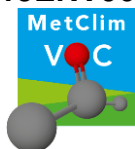
x_{mix} : amount fraction of the mixture (in nmol/mol)

In Table , q_v are the readings from the MFM as a percentage of the range of each instrument; q_{vs} are the ranges of each MFM; x_{mix} is the certificate amount fraction and x_{theo} is the theoretical value. The uncertainty of the estimated theoretical amount fraction is indicated in Table 5.

Table 4: Uncertainty budget of the theoretical amount fraction generated by dynamic dilution

Quantities/Uncertainty sources	x	u(x)	Significance Index (%)
$q_{v_{\text{mix}}}$ (%)	8.1	0.4	99 %
$q_{v_{\text{air}}}$ (%)	39.6	0.4	0 %
$q_{vs_{\text{mix}}}$ (Sml/min)	100	0.5	1 %
$q_{vs_{\text{air}}}$ (Sml/min)	5000	1	0 %
x_{mix} (nmol/mol)	10000	10	0 %
x_{theo} (nmol/mol)	40.7	2.1	5 % (k=1)

The uncertainty of the readings was estimated including the instrument certificate information and the variabilities expected due to temperature changes. The uncertainty of the amount-of-substance fraction



from the cylinder was taken from the certificate. The main sources of uncertainty are related to the instruments used and to the variability of the flow rate entering the system, mainly due to temperature deviations around the sonic nozzles upstream from the dilutor. An example of resulting uncertainty is shown in Table . For this example, negligible contributions of wall interactions was considered, as the sampling line used was a 1/8" Sulfinert tubing of 30 cm length. The uncertainty of the measurements performed by GASERA is given in this case by the certificate released by the company.

Table 5: Uncertainty of a measurement with GASERA instrument, for which the theoretical amount-of-substance fraction of the gas mixture was estimated to be 46 nmol/mol.

Quantities/ Uncertainty sources	Value [x _i]	Unit	Unc. type	Probability distribution	Divisor	Standard uncertainty [u(x _i)] (nmol/mol)
Calibrated analyser	-		B	Normal	2	5.0 %
Sampling						
		value (nmol/mol)			nmol/mol	relative (%)
Expanded uncertainty U [k = 2]		45.4			2.3	10.0

4. Uncertainty budget of Medusa-GC-MS measurements of halogenated VOCs

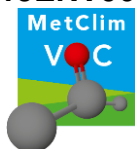
Empa and METAS identified the main uncertainty sources for halogenated VOC measurements using a preconcentration Medusa-GC-MS system. In this case, uncertainties related to sampling can be neglected. There is no adsorption on the lines and water removal and ozone traps have no influence on the quality of the measurements. The sampling conditions (e.g. sampling volume, sample pressure and sample temperature) are the same for the measurement of a sample and a standard, therefore the uncertainty of the sampled volume can be neglected, as well as the uncertainty of the instrument resolution. The uncertainty due to the linearity of the instrument is also negligible, because of the high linearity of the instrument together with similar amount fraction levels of sample and calibration standards. Identified substantial uncertainty sources can be classified in the following two categories:

- (i) uncertainties of the calibration, which is equal to the uncertainty of the calibration standard plus the instrument precision.
- (ii) uncertainty associated to the instrumental precision of the measured sample.

Within the uncertainties of the calibration, two uncertainty sources are accounted for. First, the uncertainty of the accuracy of the prepared standard tanks (u_{ACC}). This uncertainty considers the contributors related to the preparation process of the standards – such as impurities of the pure substance, uncertainty of the balance and impurities of the matrix gas – and the propagation uncertainty. The latter takes into account the measurement repeatability of each step of the hierarchical sequence of standards used in the AGAGE network. With this hierarchical sequence of standards, the amount fractions in the primary standards are propagated to the quaternary standards used on site. Second, the uncertainty associated to the instrumental precision ($u_{InstPrec}$) of the measured sample, which is estimated by bracketing each air measurement with two quaternary standard measurements.

Within AGAGE, the uncertainty of the accuracy of the primary standards (u_{ACC}) is assessed to be 3 %. In the AGAGE network, 13 gravimetric synthetic primary standards were prepared at SIO in 2005 (SIO-05) covering amount fractions around ambient levels. These primary standards are used by SIO to calibrate secondary standards, which are again used to calibrate tertiaries. Each propagation step increases the uncertainty and is considered in the uncertainty calculation. The expanded uncertainty of the SI-traceable primary standards prepared by METAS within MetClimVOC ranges from 0.8 % for CCl₄ to 2.3 % for HFC-365mfc.

The standard deviation of the standards used to bracket each air measurement is used as a proxy for the uncertainty of the instrumental precision ($u_{InstPrec}$). Medusa-GC-MS systems are calibrated by a one-point calibration, because the system is very linear and amount fractions of standards are very close to the air



measurements. In a simplified approach for estimating the measurement uncertainty of the instrument calibration, one can use the uncertainty of the standard (u_{ACC}) plus the instrument precision ($u_{InstPrec}$). For an air measurement, this uncertainty of the calibration and the uncertainty of the measurement precision needs to be considered.

The combined uncertainty of the air measurements for halogenated VOCs analysed using Medusa-GC-MS is calculated following the next simplified approach:

$$u_c(y) = \sqrt{u_{ACC}^2 + 2 \cdot u_{InstPrec}^2}$$

where,

$u_c(y)$: combined uncertainty of the air measurement (in pmol/mol)

u_{ACC} : uncertainty of the primary standard accuracy (in pmol/mol)

$u_{InstPrec}$: uncertainty of the instrumental precision (in pmol/mol)

The expanded uncertainty of the air measurement is obtained by multiplying the combined uncertainty by a coverage factor of 2 ($k = 2$). METAS prepared an example of the measurement uncertainty calculation using the simplified approach for an HFC-125 measurement. The measurement result was 29.39 pmol/mol, using METAS-2017 primary standard with a standard measurement uncertainty (u_{ACC}) of 0.26 pmol/mol. The standard and the sample were each measured five times. The instrument precision ($u_{InstPrec}$) for this measurement was 0.11 pmol/mol. The combined uncertainty of the air measurement is 0.31 pmol/mol and the expanded measurement uncertainty is 0.62 pmol/mol or 2.1 %.

Summary

During the project, several sampling methods used for VOC monitoring were evaluated. The effects of sampling line material, particle filters, water removal systems, ozone scrubbers and sorbent material in sorbent tubes were assessed. The consortium, based on the assessment findings, elaborated best practice guidelines and recommendations to sample atmospheric VOCs. Moreover, a fit-for-purpose methanol analyser was developed and a new SI-traceable reference material for PTR-MS produced by NPL was tested in the framework of the project. In both cases, guidelines and recommendations were elaborated by POLITO and UU, respectively. All these activities contributed to achieve the first part of Objective 3 regarding the evaluation and improvement of sampling and analytical methods. PTB, with the guidance of UoL, contributed to achieve the part of the objective regarding the spectral parameters. PTB conducted accurate measurements of CF_4 , SF_6 and CHF_3 , where pressure and temperature measurements were fully traceable. PTB used a dynamic dilution system allowing significantly better control over the absorber amount-of-substance fractions than the conventional mixing method. The resulting spectra will be a valuable contribution to the HITRAN database, once the findings are published. To fully achieve Objective 3, METAS with collaboration of IMTelecom, Empa and POLITO established an initial uncertainty budget for PTR-MS, GC-FID, Medusa-GC-MS and laser spectrometry.

5 Impact

In order to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium presented the project and its results 32 times at international conferences focusing on a broad range of topics, such as remote sensing, chemistry, geosciences, metrology and atmospheric monitoring, kept the project website updated (<https://www.metclimvoc.eu>), published (every two months) blog posts on the VOC measurement topic, particularly during the first half of the project and organised open training courses and workshops. The consortium was also active in social media (ResearchGate, LinkedIn and Twitter) and its activities were advertised through the EMN COO website/newsletters. A fifteen-member stakeholder committee was set up (WMO, WMO-GAW, ACE, TOAR-II, HITRAN, ACTRIS, WMO-GAW SAG-AERO, AGAGE, CREA-CEAB-CSIC-UAB Global Ecology Unit, ICOS-ATC, NILU, WMO SAG-RG, ASF KIT-IMK, ETHZ Zenobi Group), which was informed every 3 months about the progress achieved.

The final stakeholder workshop (March 2023) was organised as a satellite event of the International Congress of Metrology (CIM2023), which was held together with Global Industry 2023 in Lyon (France). Sixty participants



attend the half-day workshop, which was divided into two sessions. During each session, the consortium and some of the project collaborators presented the main outputs of the project. Each session finished with a round table where stakeholders discussed two topics: "Can SI-traceability be achieved at atmospheric monitoring stations? – needs and challenges" and "Metrology for atmospheric monitoring – uptake and further steps". Oral presentations and round-tables were recorded and the videos were uploaded to the project webpage. This enhanced the dissemination of the project results to internal and external industrial stakeholders.

Impact on industrial and other user communities

To facilitate the uptake of the new primary reference gas mixtures, working standards and other project outputs by the industry, the consortium actively searched for collaborations with gas, tubing and instrument manufacturers. In addition to the Mediterranean Center for Environmental Studies CEAM (research institute), the collaborators were Fine Metrology, Swagelok Switzerland, Ionicon, Aerodyne Research and Gasera. These manufacturers were able to apply the project outputs to ensure the robustness of their analytical devices and the accuracy of their reference materials. This created impact by enhancing the trust of buyers on the new products, which may translate into an increased market demand. One example of this was the collaboration between Gasera and a member of the consortium to develop a new methanol analyser, taking into account the project findings regarding objective 3. This collaboration also allowed the metrological characterisation of the new analyser, which will enhance buyers' trust once the analyser is commercialised. Another impact of the project on industrial communities (not only project collaborators) was the insight into quality and problematic of formaldehyde analysers provided by the results of the formaldehyde comparison organised by the consortium. Several industrial and atmospheric researchers participated in this comparison with their own instruments. Participants compared the performance of the different analysers.

The active involvement of several partners from the consortium with atmospheric monitoring networks (e.g. AGAGE, ACTRIS, WMO-GAW), together with the implication of these networks in the project stakeholder committee, will facilitate the uptake of fit-for-purpose outputs (e.g. working standards, best practice guides and recommendations). The uptake will create impact on the atmospheric monitoring communities by supporting the harmonisation of data across Europe for the long-term monitoring of climate and air quality and by ensuring the traceability and accuracy of measurement results. The development of a user-friendly on-line tool to calculate uncertainties of the VOC measurements and its distribution among the monitoring stations contributed to the project impact on these communities. Furthermore, thanks to the progress achieved during the project concerning reference gas mixtures of halogenated VOCs at low amount-of-substance fractions (few pmol/mol), one member of the consortium was designated as the Central Calibration Laboratory for ten halogenated VOCs within the WMO-GAW programme. This is a clear impact on atmospheric monitoring communities.

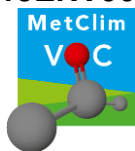
Accurate VOCs reference gas mixtures are also of high interest for breath analysis used for medical diagnostic (biomarkers). The production of such gas mixtures were presented to the *Exhalomics* community as well during a visit to one of the consortium members. This presentation rose awareness of the important role that metrology could play in the *Exhalomics* projects. For example, by providing SI-traceable RGMs of VOCs that may be present in the breath at very low amount fractions, which could improve the accuracy of breath analysis.

Impact on the metrology and scientific communities

This project fully aligns with the goals of the European Metrology Network (EMN) "Climate and Ocean Observation" by bringing together several NMIs/DIs with high priority stakeholders (identified in EMPIR JNP 18NET04 ForClimateOcean), which enhances direct uptake by end-user communities. The outputs of the MetClimVOC project were used as input for the EMN strategic research agenda and further sustainable collaboration with key-stakeholder are foreseen in this framework.

One of the partners participated actively in EURAMET TC-IM 1449 towards the development of guidelines on data management plans and on research data management for EMP projects. The project MetClimVOC was selected for the technical committee as a case study and example to follow by coordinators to elaborate and follow data management plans.

For the scientific communities, impact was created by enabling traceable, high quality and long-term harmonised atmospheric measurements, which will facilitate the assessment of long-term climate and air quality trends. Moreover, the project parametrised and improved the accuracy of spectral intensity measurements, which will benefit remote sensing facilities and databases and generate impact by predicting



spectral intensities in frequency regions where actual spectroscopic measurements of spectral intensities were not possible. The consortium started creating impact through knowledge transfer by publishing three research papers in peer-reviewed journals [1, 2, 3]. Four popular press articles – in the WMO-GAW letter number 81, ACTRIS newsletter number 19 and Contrôles Essais Mesures (CEM) numbers 82 and 83 – and periodic blog posts on the project webpage will create additional impact not only on the metrology and scientific communities, but also on the non-specialised public. Under knowledge transfer, the consortium also uploaded several training videos in the project webpage. Furthermore, the consortium started its contribution to other research projects and programs (e.g. TOAR-II) to enhance its impact. To increase the impact on scientific communities, the project actively participated in conferences and research groups out of Europe. For example, the project experts on remote sensing contribute to the discussion on spectral quality and metrology in HITRAN database. Their findings on CCl_4 and SF_6 spectra will be considered for contribution to HITRAN database as soon as the submitted manuscripts are published in peer-review journals. Moreover, the contribution of the consortium, which covered the topic of new SI-traceable RGMs of VOCs, to the Mediterranean Geophysical Union conference was submitted to a special issue on contributions to the conference, which will be published in Earth System and Environment.

Impact on relevant standards

The consortium disseminated its findings through new or revised guidelines and recommendations with their active participation in several working groups (e.g. CEN/TC264/WG12, ISO/TC158, new WMO-GAW measurement guidelines). The project created impact on standards by presenting the project activities at the EURAMET TC-MC (Metrology in Chemistry), CEN TC 264 Air quality (WG13) and AQUILA (WG7) meetings. In addition to the active presentation of project outputs at CEN-TC 264 Air quality (WG13), discussions on the use of best sampling materials and sampling conditions based on MetClimVOC inputs have taken place with this standard body. Furthermore, the priority list of VOCs selected at the beginning of the project was suggested (currently under consideration) for inclusion in the "Proposal for a revision of the Ambient Air Quality Directive (AAQD)". The consortium also provided input to the revised and new WMO-GAW Measurement guidelines that are being elaborated by the WMO-GAW VOC Expert Team. Finally, a GAW-TECH QA/QC training workshop took place in September. During the workshop, project results (which will be included in the mentioned guidelines) were presented.

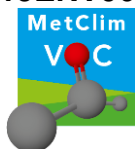
Longer-term economic, social and environmental impacts

Many economic activities will be affected by climate change leading to economic losses. Human health impacts associated with current air quality and climate change trends are also expected to place additional economic stress on health and social support systems. The outputs of this project resulted in more accurate and harmonised data that will improve the identification of climate and air quality trends. This will lead to the adoption of more effective mitigation strategies, which will generate long-term economic impact by decreasing the costs related to air pollution and climate change. Besides, effective mitigation policies will create environmental impact by limiting the use and emissions of VOCs through more strict legislation and treaties. The future harmonised datasets will additionally lead to a better understanding of long-term global VOC emissions and of the chemistry involved by the scientific community.

6 List of publications

- [1] Sassi, G.; Khan, B.A.; Lecuna, M. Reproducibility of the quantification of reversible wall interactions in VOC sampling lines. *Atmosphere* **2021**, 12, 280. <https://doi.org/10.3390/atmos12020280>
- [2] Worton, D.R.; Moreno, S.; O'Daly, K.; Holzinger, R. Development of an International System of Units (SI)-traceable transmission curve reference material to improve the quantitation and comparability of PTR-MS measurements. *Atmospheric Measurement Techniques* **2023**, 16, 1061-1072. <https://doi.org/10.5194/amt-16-1061-2023>
- [3] Persijn, S.T. and Baldan, A. A new look at the sorption kinetics in reference gas standards. *Measurement Science and Technology* **2023**, 34, 115018. <https://doi.org/10.1088/1361-6501/ace9ee>

This list is also available here: <https://www.euramet.org/repository/research-publications-repository-link/>



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