European Metrology Programme for Innovation and Research

Delivering Impact

Courtesy, Fine Metrology

The **WaferCAL permeation tubes**

Providing measurement traceability for selected volatile organic compounds

Thousands of volatile organic compounds (VOCs) are present in the air. Whilst most are harmless some have direct or indirect negative effects on air quality, climate change and environment. These are monitored by atmospheric networks, but at the start of 2020 reference gases for calibrating station instruments were missing, meaning measurements lacked measurement uncertainty or robust links to the international system of units (SI).

Europe's National Measurement Institutes working together

The European Metrology Programme for Innovation and Research (EMPIR) has been developed as part of Horizon 2020, the EU Framework Programme for Research and Innovation. EMPIR funding is drawn from 28 participating EURAMET member states to support collaborative research between Measurement Institutes, academia and industry both within and outside Europe to address key metrology challenges and ensure that measurement science meets the future.

Challenge

Thousands of volatile organic compounds (VOCs) are present in the atmosphere. Of those, halogenated ones containing fluorine, chlorine, or bromine - are mainly emitted by anthropogenic activities. In 1987, after it was discovered that chlorofluorocarbons used in refrigeration were destroying the protective ozone layer, the Montreal Protocol was established, banning their use. Due to this ban, and following ones such as the Kyoto protocol, new halogenated compounds replacing the banned ones have continuously emerged. Although these are at very low atmospheric amount fractions (pmol- nmol), and do not all contribute directly to climate change, their source, intermediate and degradation products are very long-lived and have a negative impact on the environment.

One such is 1,2-dichloroethane, widely used in industry as a solvent, has been linked to ozone layer depletion. Its atmospheric levels are currently monitored at several sites of the Advanced Global Atmospheric Gases Experiment (AGAGE). This network also monitors the levels of another halogenated VOC, hexafluroro-2-butene, which is drawing concern because of its potential toxicity to certain terrestrial and marine species when decaying into trifluoroacetic acid.

However, due to the reactivity of some halogenated VOCs, or new emerging ones produced by industry, no SI-traceable reference gases existed for these at atmospheric levels, meaning that measuring instruments remained uncalibrated and lacked measurement uncertainty budgets.

Solution

During the MetClimVOC project, reference gas mixtures containing six halogenated VOCs were identified as being relevant for the atmospheric community - difluoromethane (HFC-32), pentaflurobutane (HFC-365mfc), dichloromethane (CH_2Cl_2), tetrachloromethane (CCl_4), 1,2-dichloroethane, and hexafluoro-2-butene (HFO-1336mzzZ). These were produced by METAS based on the permeation dynamic method described in the international standard ISO 6145-10.

Permeation tubes containing a polymer membrane were pre-conditioned at selected temperatures and pressures for at least one week and calibrated using METAS' magnetic suspension balance. The VOC of interest was then added at a defined volume or mass and eluted into a stream of high purity synthetic air. Each gas was then cryo-filled into passivated cylinders using an improved technique with traceability provided by the volumetric standard of Switzerland.

References gas mixtures were produced with amount-of-substance fractions from 1.0 pmol/mol for hexafluoro-2-butene to 74.6 pmol/mol for tetrachloromethane, with expanded uncertainties < 3% and at least 18 months temporal stability.

Impact

For over 30 years, Fine Metrology has provided high-quality sources for calibrating gas analysers and air quality measuring instruments used worldwide for environmental monitoring, industrial safety, scientific research, and manufacturing quality.

Due to their expertise, Fine Metrology became collaborators in the project, developing new permeation tubes for the selected halogenated VOCs following the consortium's requirements. These permeation tubes, of high purity (>99%), such as the company's WaferCAL tubes, were made commercially available for generating the source used to produce the halogenated VOC reference gas mixtures. These gas mixtures, at ambient levels, are now available for monitoring networks such as AGAGE, ensuring that measuring instruments can be accurately calibrated with, clear SI traceability.

The extensive testing performed by Fine Metrology to produce fit-for-purpose permeation tubes, including how to condition and calibrate these, has allowed them to improve their accuracy and reproducibility, information they can now incorporate into new products.

The new reference gases will allow more accurate monitoring of these pollutants and, in the long-term, the adoption of more effective mitigation strategies to protect both human health and the environment.

Providing SI-tracebility for volatile organic species

The MetClimVOC project:

- Determined a priority list of oxygenated VOCs, terpenes and halogenated VOCs. Except for the latter, the listed VOCs were incorporated into the Air Quality Directive (EU) 2024/2881.

- Produced first SI-traceable reference gas mixtures for oxy-VOCs acetone, ethanol, butanone and methacrolein at low amount fractions (< 100 nmol/mol) with a temporal stability up to 18 months.

- Developed four protocols for generating SI-traceable working standards for oxy-VOCs, two for terpenes and one for halogenated VOCs.

- Developed an on-line tool to simplify uncertainty budget calculations for the atmospheric monitoring community.

- Investigated effects of line material, particle filters, water removal, ozone scrubbers and sorbent tubes on sampling.

- Developed a methanol analyser and contributed to the development of new SI-traceable reference material for Proton-Transfer-Reaction Mass Spectrometry.

- Obtained SI-traceable spectral parameters for tetrafluoromethane, sulfur hexafluoride and fluoroform to be provided to HITRAN, a database to predict and simulate the transmission and emission of light in the atmosphere.

The improved and harmonised data will allow better mitigation strategies aimed at decreasing the health and environmental burden related to air pollution and climate change.

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

www.euramet.org/project-19ENV06

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11326/09/25- 19ENV06