Standardizing atmospheric measurements of halogenated VOCs based on SI-traceability

Diana Roos, Tobias Bühlmann, Martin K. Vollmer, Florentin Hiault, Emmanuel Mahieu, Stefan Reimann

Abstract

- METAS contributes to the Global Atmosphere Watch (GAW) programme by serving as Central Calibration Laboratory (CCL) for ten halogenated volatile organic compounds (VOCs).
- GCOS-CH project SI-haloVOCs: Standardizing long-term remote sensing and in situ measurements of atmospheric halogenated VOCs based on SI-traceability.

Introduction

- Many halogenated VOCs are **potent greenhouse gases**, contribute to **stratospheric ozone depletion** and/or form degradation products that can **harm the environment.**
- They are classified as **Essential Climate Variables** by GCOS and many of them are regulated under international agreements (e.g. Montreal Protocol).
- Atmospheric monitoring is essential for understanding climate change and to define and review mitigation strategies. To support comparable and accurate data, we developed SI-traceable standards for these compounds.

GAW-CCL for ten halogenated VOCs

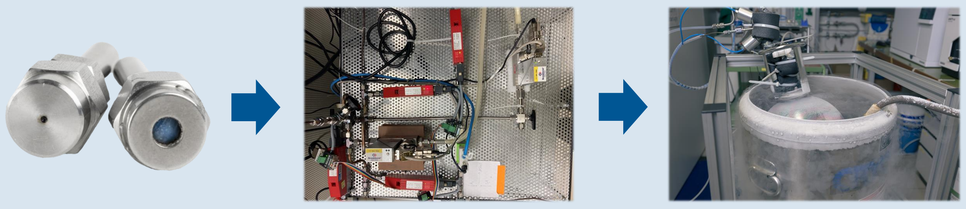
GAW: Long-term global programme of the World Meteorological Organization (WMO) that coordinates observations of the atmospheric composition and its changes.

CCL: Responsible for maintaining and distributing the GAW references for instrument calibration for a specified variable. All measurements within GAW must be traceable to the CCL standards. Since June 2023, METAS is the GAW-CCL for ten halogenated compounds. METAS CCL services include:

Hosting the GAW primary standards for:

CH_2Cl_2	HFC-365mfc	HFO-1336mzz(Z)	CFC-13	HFO-1234yf
CCl_4	HFC-32	1,2-dichloroethane	HFC-132b	HFC-125

Production method of SI-traceable standards at atmospheric levels:



Permeation | Dynamic dilution | Cryo Filling

Secondary standards for calibration purposes:

spiked Rigi whole air

Long-term stability assessment of the standards. First tests after 2.5 years:

SilcoNert®2000 coated Essex

uncoated stainless steel

Compounds list extension:

Within projects such as SI-haloVOCs, new standards are being developed for halogenated VOCs that are detected in the atmosphere but for which SI-traceable reference gas mixtures are lacking.

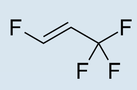
GCOS-CH project SI-haloVOCs

Aim 1: **In situ quantification** of two environmentally relevant halogenated VOCs that currently lack SI-traceable reference gas mixtures.

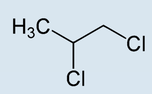
Aim 2: **Full comparability of in situ and remote sensing** records for two potent greenhouse gases, HFC-23 (CHF_3) and PFC-14 (CF_4), by linking the 30-year remote sensing (NDACC) and 20-year in situ (AGAGE) records at Jungfraujoch (JFJ) to the International System of Units (SI).

SI-traceable standards are produced with expanded uncertainties < 3 % for:

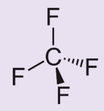
HFO-1234ze(E)



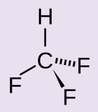
1,2-dichloro-propane



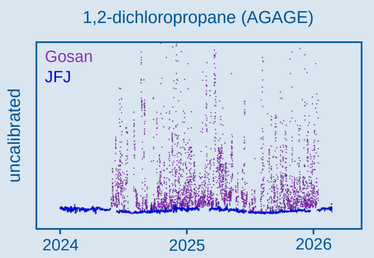
PFC-14



HFC-23



First quantification of HFO-1234ze(E) and 1,2-dichloropropane:



Remote sensing FTIR:

A retrieval tool for remote sensing measurements of PFC-14 and HFC-23 is used by implementing SI-traceable cross-sections.

Direct comparison of JFJ long-term records thanks to SI-traceability:

In situ GC-MS | Remote sensing FTIR

Outlook: The METAS CCL for ten halogenated VOCs is now established, forming the basis for GAW measurements. CCL references already enable quantification of key halogenated VOCs at AGAGE stations. Next steps include continued long-term stability studies and linking the METAS CCL to the European Calibration Center to be established at University of Bristol (project REIGN-MP).

Impact: Increased worldwide coverage of comparable measurements through the link to the SI.

Quantification of newly detected halogenated VOCs in the atmosphere.

Inclusion of four additional compounds to the METAS GAW-CCL list.

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Contact: tobias.buehlmann@metas.ch, diana.roos@metas.ch