ACTRiS

CiGas

Implementation Status

Germany | France | Finland | Switzerland | Germany

NOx/VOC QA workshop 2023; Online – April, 17th - 19th 2023

This project receives funding from the European Union's Horizon 2020 research and innovation programme under grant agreements No 654109 and 739530

Activities

Management and coordination

- Monthly management meetings
- Annual CiGas Community workshop
- Participation in RIComm and CF-Meetings; other working groups

Links with associated communities

- Standards Committee CEN WG13: „Ambient air - Ozone precursors and benzene”
- TOARII
- WMO-GAW: WCC for VOC
- MetClimVOC
- CAMS-21a-2nd phase; RI-URBANS; ATMO-ACCESS; EQUIPEX OBS4CLIM

Consultancy for NMHCs
Trainings for NMHCs measurement and data evaluation (planned 2023)
Ready for NMHC working standard and target gas checks

ACTRiS CiGas

Available scales

NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

UKAS REFERENCE MATERIALS 4002

Certificate of Calibration

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D933529

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **Forschungszentrum Jülich GmbH**

ADDRESS: Institut IEK-8: Troposphäre, Wilhelm-Johnen-Strasse, 52425 Jülich, Germany

CALIBRATION DATE: 08 December 2020

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)	Component	Amount fraction / (nmol/mol)
Ethane	4.24 ± 0.13	2-methylpentane	4.39 ± 0.09
Ethene	4.15 ± 0.09	*n*-hexane	4.39 ± 0.09
Propane	4.18 ± 0.09	Isoprene	4.37 ± 0.09
Propene	4.15 ± 0.09	*n*-heptane	4.40 ± 0.09
2-methylpropane	4.26 ± 0.11	Benzene	3.72 ± 0.08
n-butane	4.22 ± 0.09	2,2,4-trimethylpentane	4.13 ± 0.09
Ethyne	4.37 ± 0.22	*n*-octane	4.14 ± 0.09
trans-but-2-ene	4.23 ± 0.09	Toluene	3.61 ± 0.10
But-1-ene	4.21 ± 0.09	Ethylbenzene	3.91 ± 0.10
cis-but-2-ene	4.22 ± 0.09	*m*-xylene + *p*-xylene	7.60 ± 0.20
2-methylbutane	4.16 ± 0.09	*o*-xylene	3.74 ± 0.10
n-pentane	4.18 ± 0.09	1,3,5-trimethylbenzene	3.80 ± 0.10
1,3-butadiene	4.27 ± 0.09	1,2,4-trimethylbenzene	3.83 ± 0.10
trans-pent-2-ene	4.20 ± 0.09	1,2,3-trimethylbenzene	3.80 ± 0.10
Pent-1-ene	4.27 ± 0.09	Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 5 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2021030009-1 **Date of issue:** 22 March 2021

Signed: (Authorised Signatory)

Name: Dr D R Worton (on behalf of NPLML)

Checked by:

NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

UKAS REFERENCE MATERIALS 4002

Certificate of Calibration

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D933592

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CUSTOMER: **Forschungszentrum Jülich GmbH**

ADDRESS: Institut IEK-8: Troposphäre, Wilhelm-Johnen-Strasse, 52425 Jülich, Germany

CALIBRATION DATE: 05 May 2021

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Toluene	3.93 ± 0.12
(+/-)-α-pinene	4.17 ± 0.21
(+)-3-carene	3.93 ± 0.20
R-(+)-limonene	3.81 ± 0.12
1,8-cineole	4.08 ± 0.21
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 1 year from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2021030009-2 **Date of issue:** 07 May 2021

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

ACTRiS CiGas

Measurement performance monitoring

Preparation for round-robins

Measurement guidelines

HOME SCIENCE & TECHNOLOGY NATIONAL FACILITIES PARTNERS & USERS ANNOUNCEMENTS & RESOURCES

Publications & documents

Standard Operation Procedures

For NOx and VOC can be found here SOP for NOx and VOC

ACTRiS

Deliverable 3.17. Updated Measurement Guideline for NOx and VOCs

Stefan Reimann (EMPA), Robert Wegener (FZJ), Anja Claude (DWD), Stephan Sauvage (CNRS)

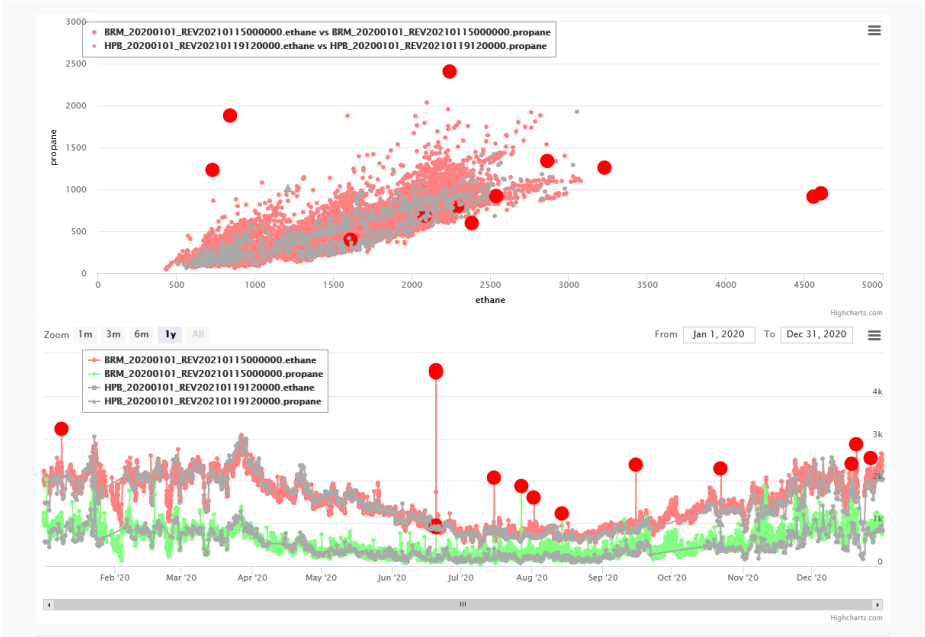
Work package no	WP3
Deliverable no.	D3.17. Updated Measurement Guideline for NOx and VOCs
Lead beneficiary	EMPA
Deliverable type	☑ R (Document, report) ☐ DEC (Websites, patent fillings, videos, etc.) ☐ OTHER: please specify .....

ACTRi CiGas

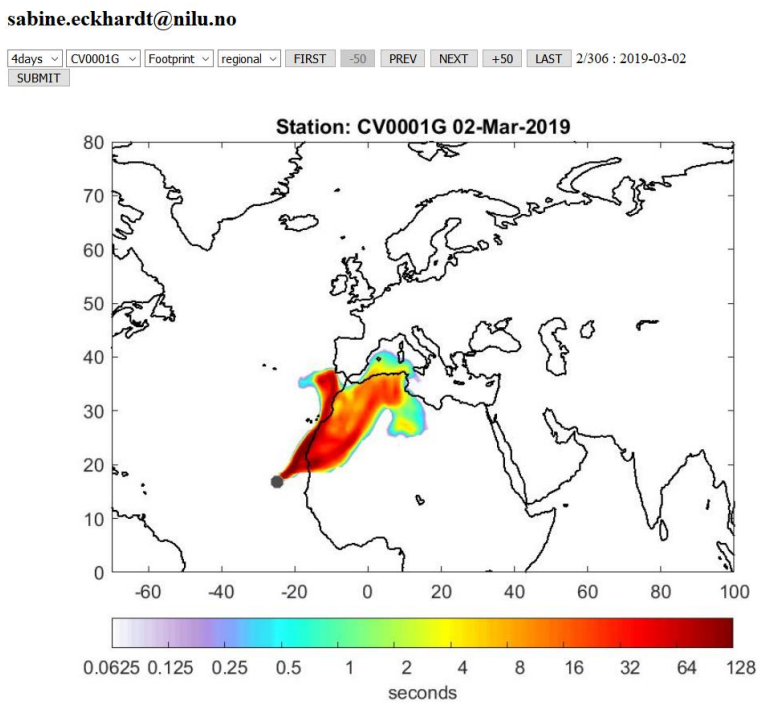
Data review

Empa
Materials Science and Technology

@VOC@



footprints



ACTRiS CiGas

Activities

Labelling

- Develop and establish workflows, communication and management
- Contribution to the assessment for NMHCs
- Reporting for labelling step 1a

Preparation for auditing pilote NFs

- Provision of gas standards
- On site audit

s-b-s-Inter comparisions

Scientific developments

- Method developments and QA procedures for CIMS & TD-GC
- Low cost sensor applications
- Airborne applications of CIMS

Implementation Status (FZJ)

VOCUS

TD-GC-FID/MS
(Gerstel TDS-G; CIS)

PTR-TOF-MS
8000

Liquid
Calibration Unit
Certified
laboratory
standards (NPL)

Diffusion sources

Implementation Status (FZJ)

System for automated Canister and sample tube analysis connected to TD-GC-FID/MS (Markes, Agilent)

On-line TD-GC-FID/MS (Markes, Agilent)
TD-GC-MS (Markes, Agilent)

Gas mixing and continuous calibration gas generation

Calibration flow tube (CACTUS)

Implementation Plans (FZJ)

Upcoming:

- Gas mixing & cylinder filling → Working standard provision
- Target gas filling → Compressor
- PTR-TOF-MS (FUSION)
- HCHO TILDAS Instrument
- Hands-on training center + s-b-s-intercomparison facility connected to SAPHIR and JULIAC

Implementation status (Overview)

Activity	NMHCs	Implementation year
Consultancy	anthropogenic	Available
	biogenic	2024
Training	anthropogenic	2023
	biogenic	2024
Measurement Guidelines	anthropogenic	Available
	(update)	2023
	biogenic	2024
Scale available at NFs	both	Available
Working standard checks	anthropogenic	Available
	biogenic	2024
Measurement performance monitoring	anthropogenic	2023
	biogenic	2025
Data review	anthropogenic	Available
	biogenic	2024
Analytical instrument compatibility test	both	2025
Audits	anthropogenic	2023
	biogenic	2024
ACTRIS approved new technologies	both	2025

FZJN Implementation

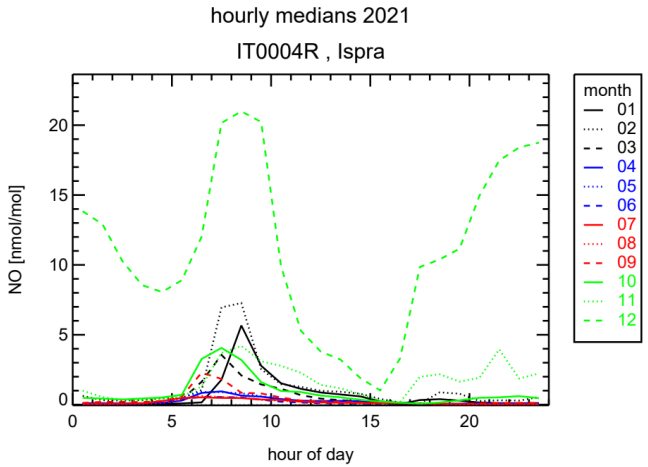
Challenges

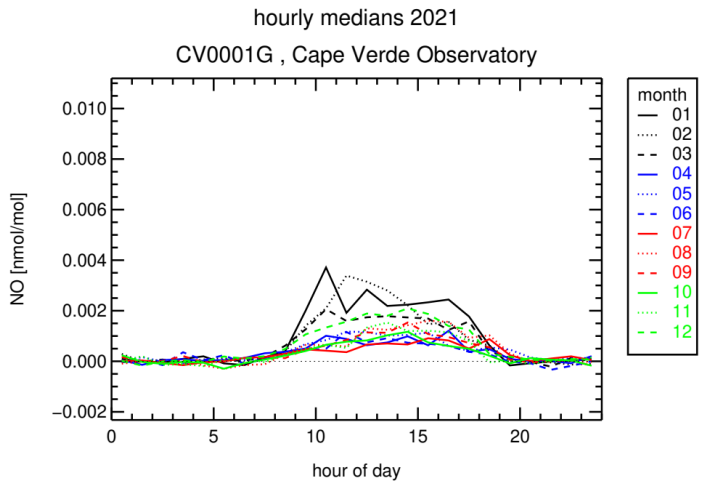
NO:

Traceable gas standard available from CCL

NO level span three orders of magnitude (!) at different ACTRIS sites

Most Sensitive CL reference instrument will be purchased
(April 2023)





FZJN Implementation

Challenges

NO_2

Traceable gas standard available from CCL

NO level CLD Measured after conversion into NO is prone to interferences

Setup of:

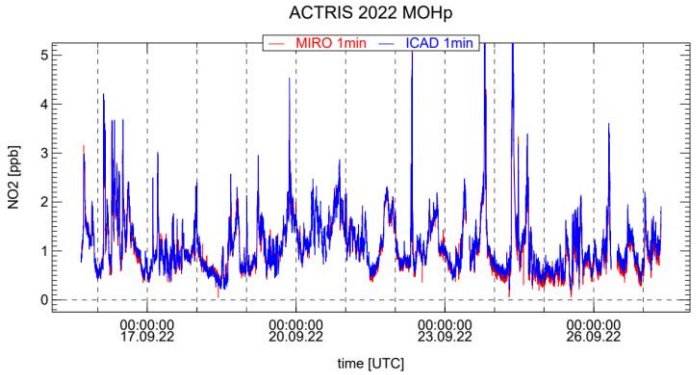
Spectroscopic (direct!) reference method for direct NO2

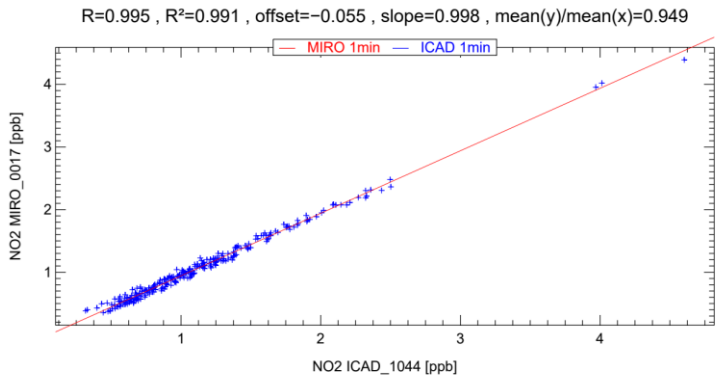
measurement onsite (mobile !)

DOAS instruments operating.

First deployment at campaign at Hohenpeissenberg shows excellent performance

DOAS spectrometers





Comparison of FZJN DOAS with TDL spectrometer at Hohenpeissenberg

FZJN Implementation

Challenges

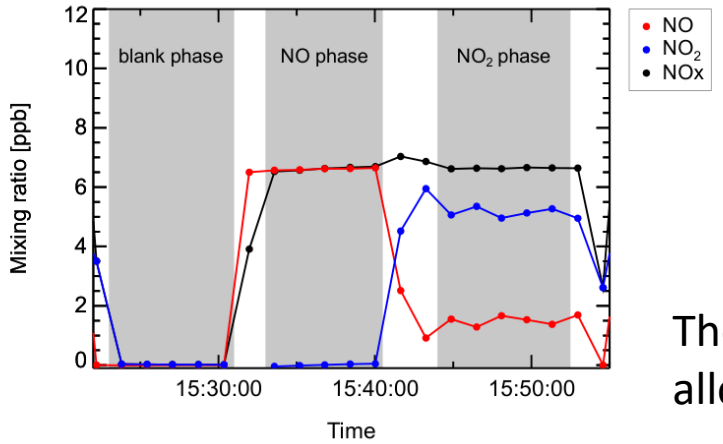
NO_2

No traceable NO_2 gas standard available

NO_2 for calibration is produced from NO and ozone

Setup of:

Mobile calibration stand with a gas phase titration and humidification device and NO / NO_2 and CO_2 measurements for checking NF devices by measurements on site. Calibration stand set up., will be replicated in 2023.



Mobile Calibration Unit

The rack will also contain ozone and water measurements allow to check for interferences at the NFs

FZJN Implementation

SAPHIR

SAPHIR chamber with JULIAC tower

All instruments are routinely operated in parallel at ambient concentrations at SAPHIR to check for potential problems, such as interference.

Here, different techniques (CAPS, TDL, DOAD, CL) are compared to each other.

A new lab building will be setup close to the chamber to host NOx and VOC during intercomparison

Implementation Status (IMT)

IMT Nord Europe
École Mines-Télécom
IMT-Université de Lille

Available:

- PTR-QiToF-MS Ionicon
- PTRMS Kore
- TD-GC FID/FID; TD-GC-FID/MS (offline & online)
- Liquid Calibration Unit; Gas Calibration Unit
- Permeation system
- Target gas cylinder filling system
- Multi-gas generation systems & intercomparison platform

Upcoming:

- VOCUS 2023-2024

+ Certified laboratory standards (NPL, NIST, upcoming VSL)

ACTRiS CiGas

Implementation Status (DWD)

- Monitoring of reactive gases @MOHp since 1994 (GAW)
  → Monitoring of VOCs @MOHp since 1998 (GAW+EMEP)

- In ACTRIS since 2011: involved in the development of QA/QC measures, measurement guidelines and organisation of intercomparison campaigns (side-by-side and RR)

GAW measurement facility for VOCs

Monitoring at HPB:

- **VOC (>50 NMHC, BVOC, OVOC; 12h intervals; 3 GC systems):**
  - **TD-GC-FID (C2-C8 NMHCs),**
  - **TD-GC-MC/FID (biogenic VOCs),**
  - **TD-GC-FID/FID(/MS) (NMHCs+OVOCs)**
  - **PTR-TOF-MS (2023)**
- CO (cavity + fluorescence)
- O_3 (UV-absorption)
- NO (CLD)
- NO2 (CLD-PLC/BLC + CAPS)
- NOy (gold converter CLD + TD-CAPS)
- SO_2 (fluorescence)
- CO_2, CH_4, N_2O (ICOS – cavity absorption)
- OH, H_2SO_4, K(OH), ROx (CIMS)

GAW measurement facility for reactive inorganic trace gases and aerosols

Measurement of NMHCs by GC

On-Line sampling

- Inlet location >2 m above the building and >5 m above ground
- Sample path including inlet line and filters inert to NMHCs → surface passivated steel, glass
- Controlled sampling flow
- Removal of water, ozone, carbon dioxides and particles
- Sample pre-concentration (low temperature adsorption)
- Transfer of the analyte to GC (by carrier gas flow, high temp., potentially 2nd focussing trap)
- FID and/or MS detection

Off-line sampling (additional requirements with respect to on-line sampling)

- Passivated or electropolished stainless steel canisters
- Glass flasks
- Storage times max. 30 days

Data quality objectives for NMHCs measured by GC

Table 3 Data quality objectives (DQOs) for the measurements of NMHCs in whole air compressed test gases (inter-laboratory compatibility) expressed as the expanded combined uncertainty (k=2) and the repeatability (k=1; standard deviation). The basic station performance requirements correspond to the former and weaker DQOs of GAW Report 171 (2006).

	GAW basic performance expanded combined uncertainty	GAW basic performance repeatability	ACTRIS target performance expanded combined uncertainty	ACTRIS target performance repeatability
Alkanes	10%	5%	5%	2%
alkenes incl. isoprene	20%	10%	5%	2%
Alkynes	15%	5%	5%	2%
Aromatics	15%	10%	5%	2%
mole fraction [1] <100 pmol/mol	10/15/20 pmol/mol	5/10 pmol/mol	5 pmol/mol	2 pmol/mol

[1] For mole fractions below 100 pmol/mol, the DQO are expressed in pmol/mol, reference is the above stated relative value at 100pmol/mol e.g. for alkanes basic performance 10 pmol/mol.

NMHC-Gas Standard Requirements

The Central Calibration Laboratory (CCL) maintains the primary standard that defines the calibration scale. → NPL (UK)

Standard requirements for ACTRIS-NFs:

1. (secondary) **Laboratory standard:** multi-component standard (synthetic mixture), produced and certified by the CCL.

2. (tertiary) **Working standards:** Cover most (ideally all) components measured and are used for regular calibration. WS can be other-certified or custom-made synthetic mixtures, or compressed whole air, calibrated by CiGas.

3. A **target gas mixture:** Compressed whole air / synthetic mixture calibrated by CiGas.

The target gas is used to check the assigned values of the calibration mixtures and the calibration process itself, and is treated as an air sample with unknown amount fraction. Monitoring the target gas concentrations yields information about the performance of the instrument, drifts of the laboratory standard, and potential instrument problems.

Recommended frequencies for standard, blank and target gas measurements

System	Lab. Standard	Working Standard	Blank	Target gas	Stand. Addittion
GC-FID	2/year*	2/month*	1/week	1/month*	1/year*
GC-MS	2/year*	Every 2-4 samples	1/week	1/month*	1/year*

*) 3-5 replicates