OVOC working standards: Transferring metrological traceability to the field

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METAS
Empa Materials Science and Technology
IMT Nord Europe École Mines-Télécom IMT-Université de Lille
VSL National Metrology Institute
DWD
Universiteit Utrecht
LNE Laboratoire National de Métrologie et d'Essais

MetClimVOC – Metrology for climate relevant VOCs

EURAMET – EMPIR project (June 2020 – May 2023)

Consortium: 13 partners

Coordination: METAS

Overall aim: to ensure accurate worldwide comparable VOC monitoring data by improving reference gas standard quality and measurement techniques, providing complete and realistic uncertainty budgets and guaranteeing the measurements' traceability to the international system of units (SI-traceability).

EURAMET: European Association of National Metrology Institutes

EMPIR: European Metrology Programme for Innovation and Research

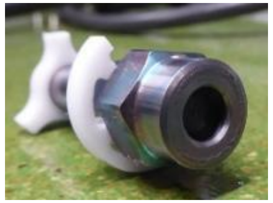
MetClimVOC – Metrology for climate relevant VOCs

- **Objective 1**

  To develop new accurate and stable reference gas standards at low amount fractions for priority VOCs:

  - oxy-VOCs, terpenes: 1 – 1000 nmol/mol, expanded uncertainty < 5 %
  - halogenated VOCs: < 1 nmol/mol, expanded uncertainty < 3 %

Dynamic reference gas standards



Static reference gas standards

(Source: VSL)

MetClimVOC – Metrology for climate relevant VOCs

- **Objective 2**

  To define, select and validate fit-for-purpose protocols for preparing SI-traceable working standards and calculating their uncertainty budget.

OVOC SI-traceable working standards – overview

Target compounds

- **Acetaldehyde**
- **Acetone**
- Ethanol
- Methacrolein
- **Methanol**
- **MEK**
- MVK

High diversity of instruments and calibration methods

Detailed description in Iturrate-Garcia et al. (2025)

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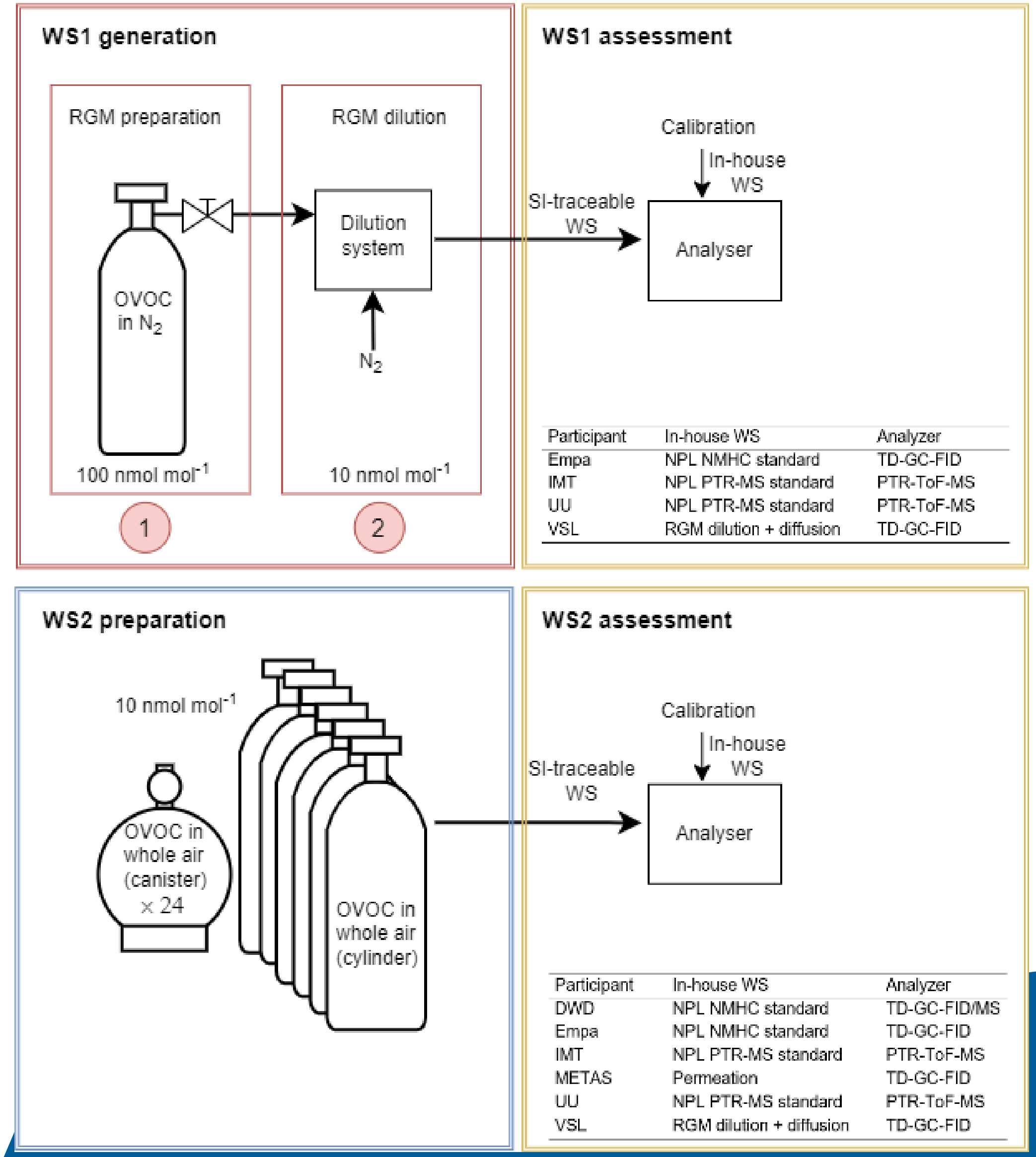
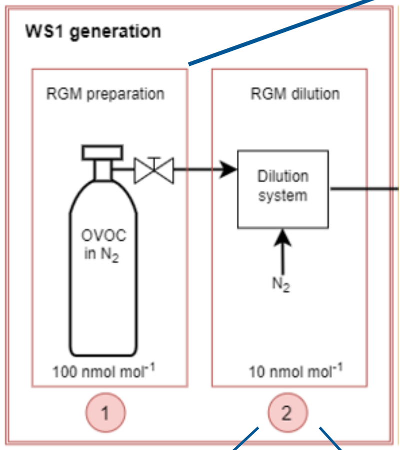
Dataset DOI: https://doi.org/10.5281/zenodo.14178374

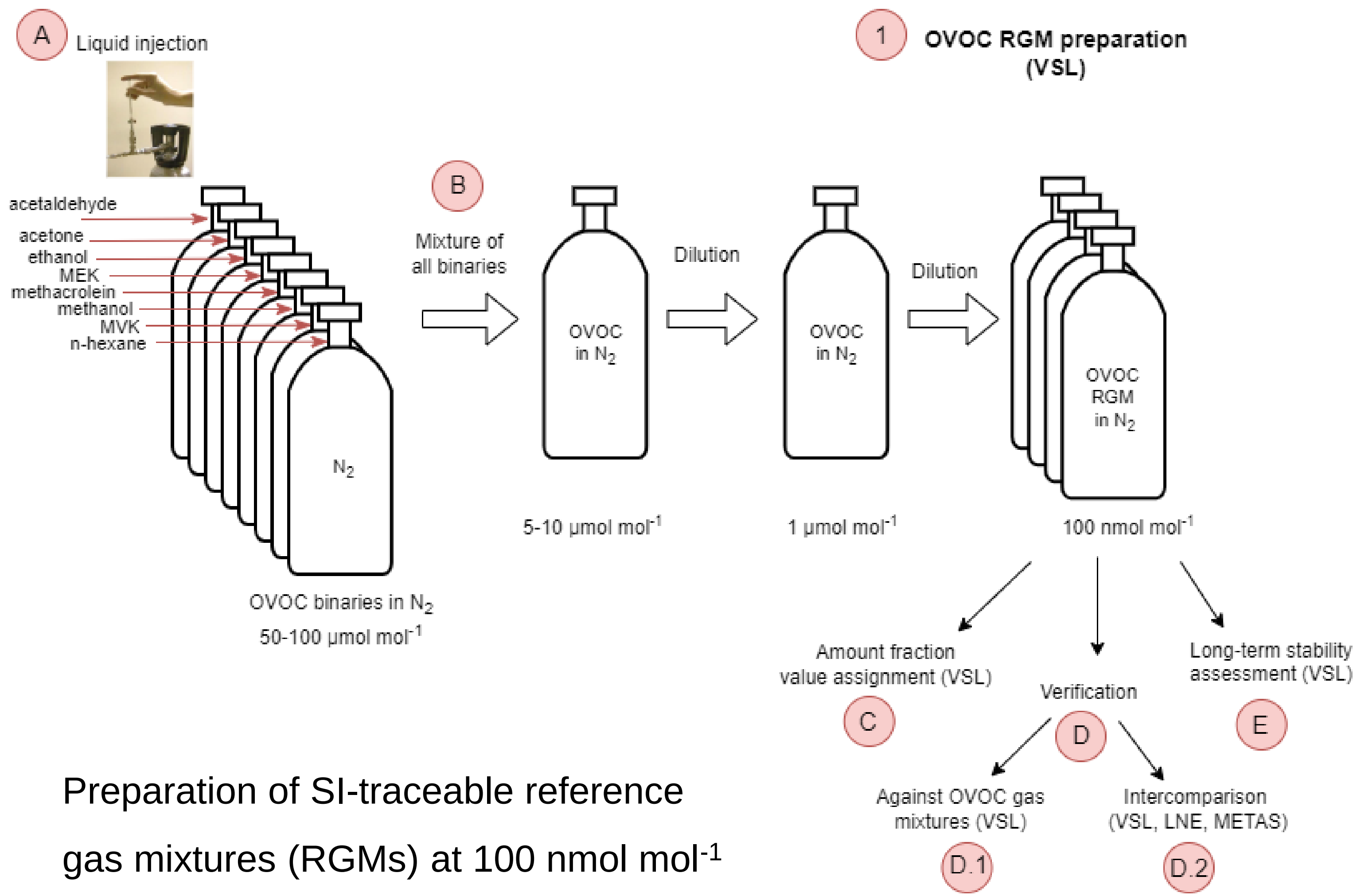


Dilution of reference gas mixtures (WS1) – methodology



VSL dilution system

METAS dilution system (VeRDi)



Preparation of SI-traceable reference gas mixtures (RGMs) at 100 nmol mol^{-1}

RGM value assignment

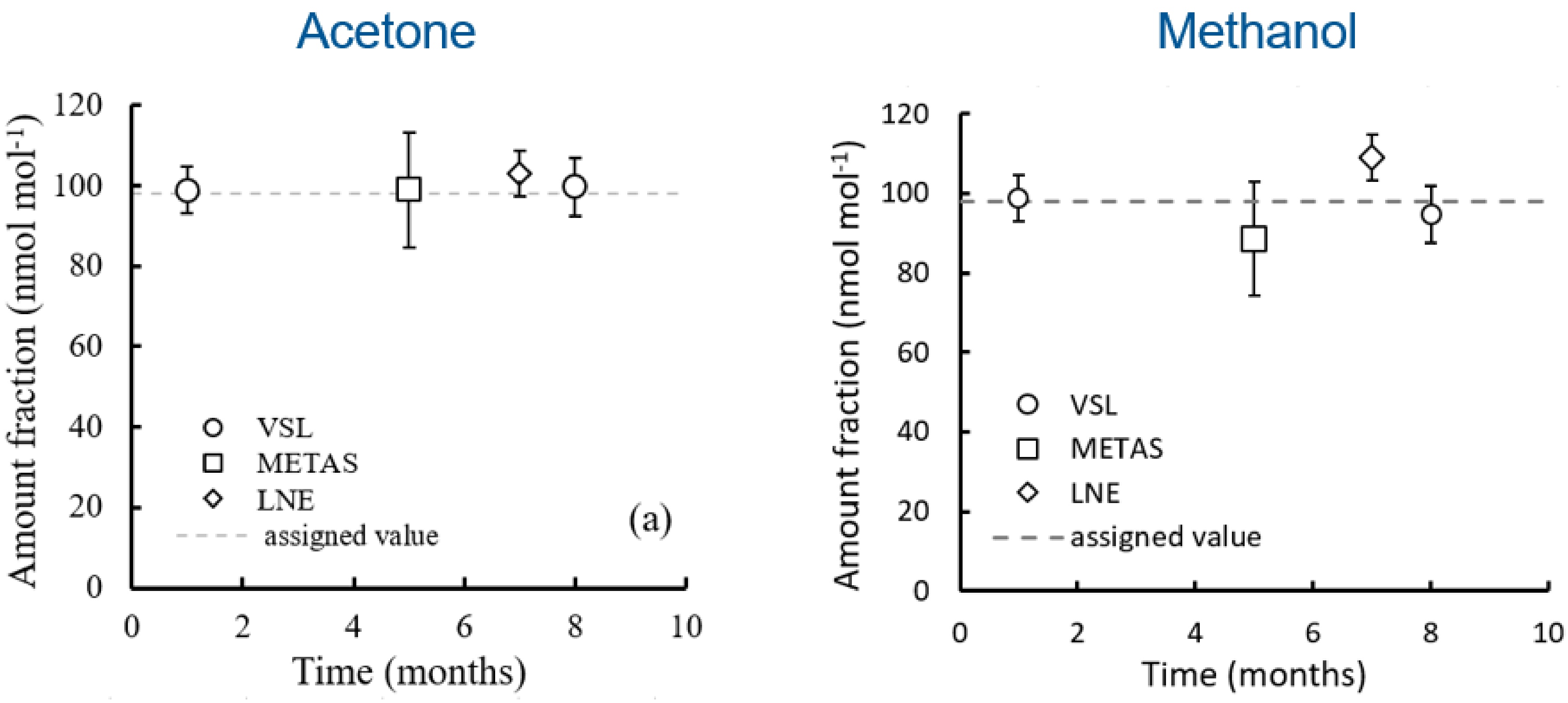
Value assignment based on gravimetry except for methanol and ethanol (analysis against dynamic RGMs based on diffusion)

RGM code	$x_i \pm U$ (nmol mol^{-1})						
	Acetaldehyde	Acetone	Ethanol	Methacrolein	Methanol	MEK	MVK
VSL221418	103.1 ± 2.6	98.1 ± 1.6	98.0 ± 2.4	100.7 ± 1.6	98.0 ± 3.4	100.2 ± 1.8	101.8 ± 3.0
VSL221419	101.9 ± 2.1	99.3 ± 2.2	99.2 ± 3.2	99.6 ± 2.5	99.2 ± 5.3	99.1 ± 2.5	100.7 ± 4.3
VSL221420	103.3 ± 9.6	97.9 ± 4.4	93.3 ± 3.8	101.0 ± 4.2	99.8 ± 6.8	100.4 ± 3.9	102.1 ± 3.6
VSL221421	101.2 ± 9.5	99.9 ± 3.6	96.6 ± 5.0	99.0 ± 4.1	105.1 ± 5.0	98.4 ± 3.4	100.0 ± 5.8

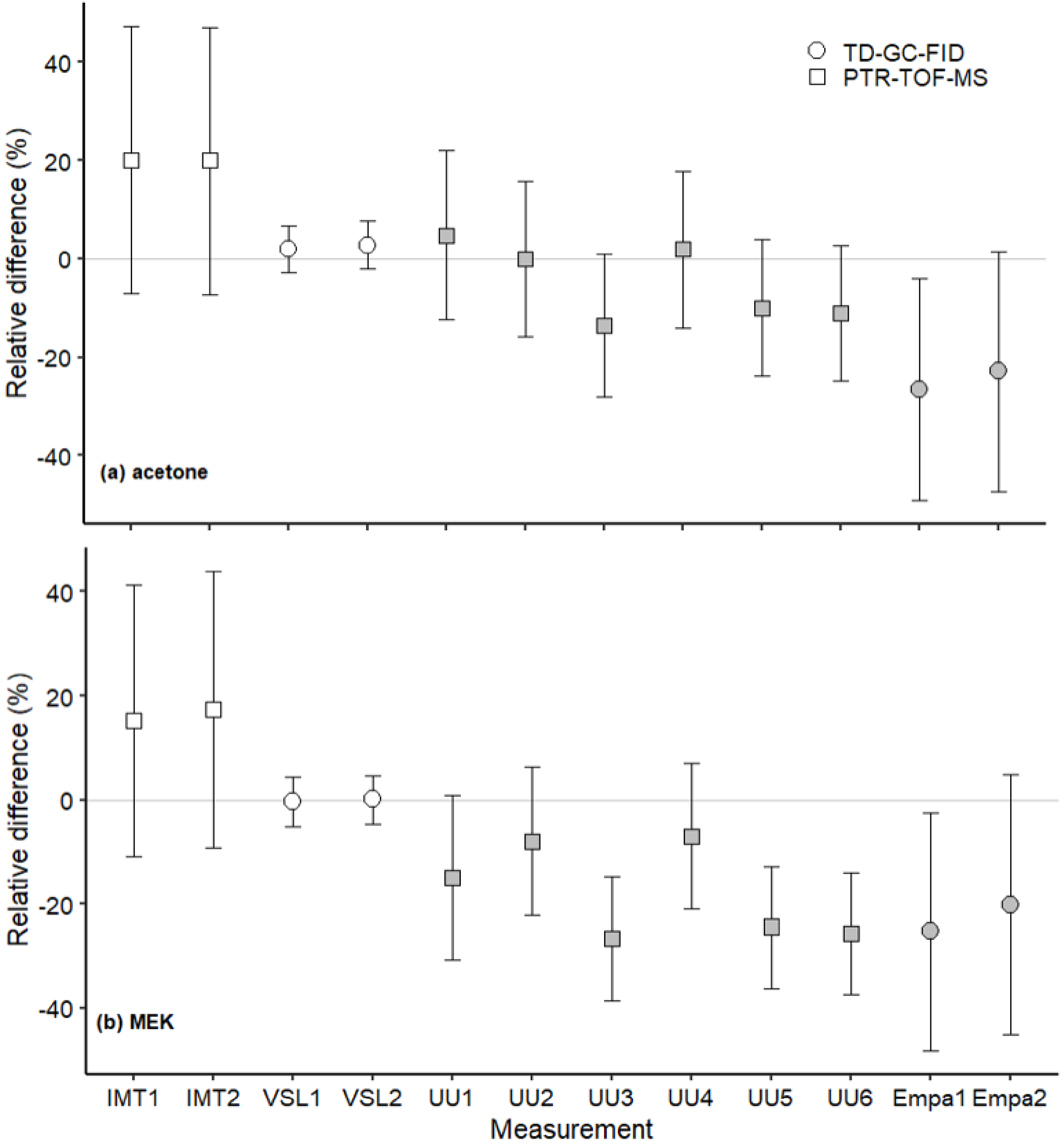
RGM verification

RGM verification against OVOC gas standards and through an intercomparison

RGM long-term stability

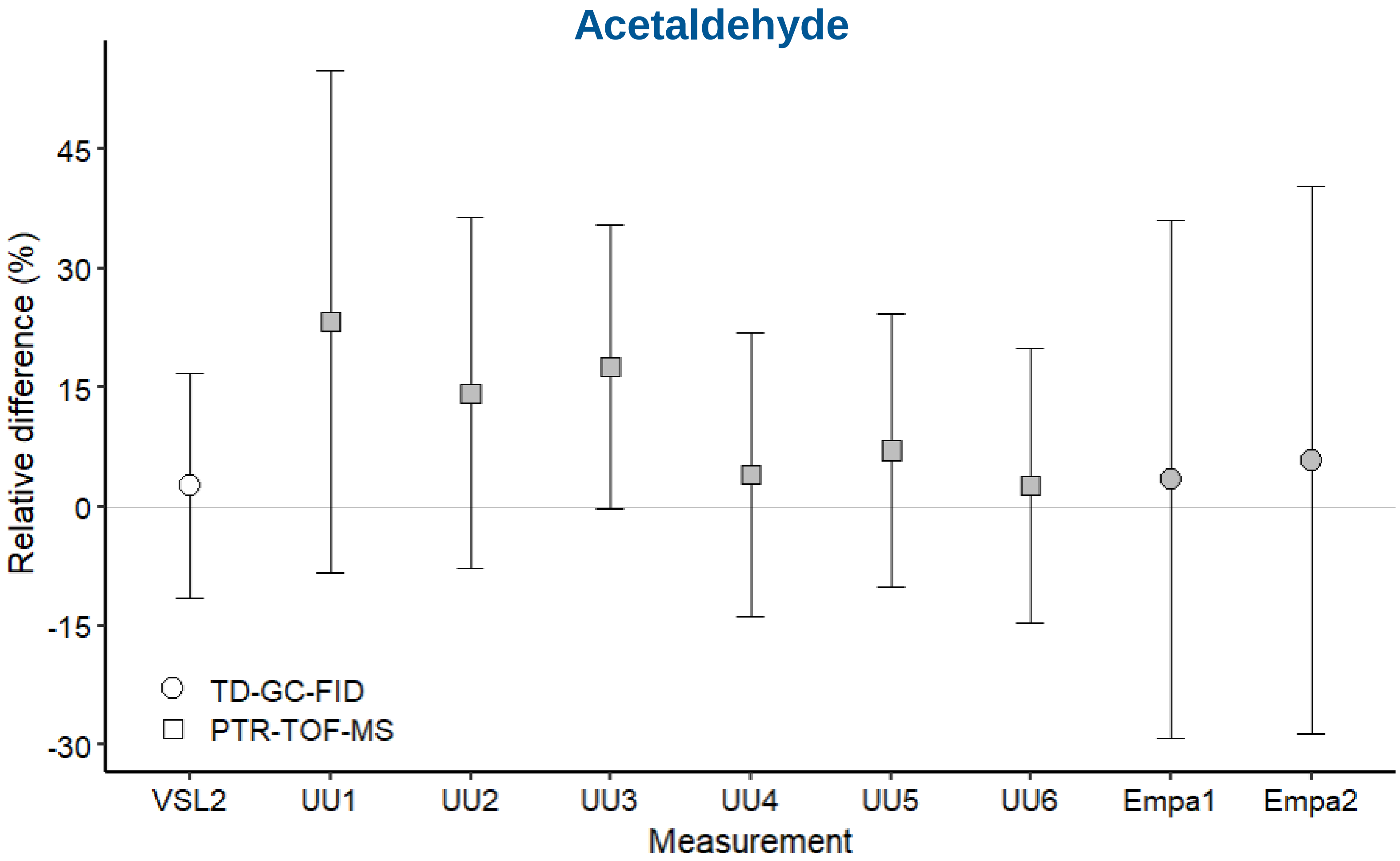


Dilution of reference gas mixtures (WS1) - results

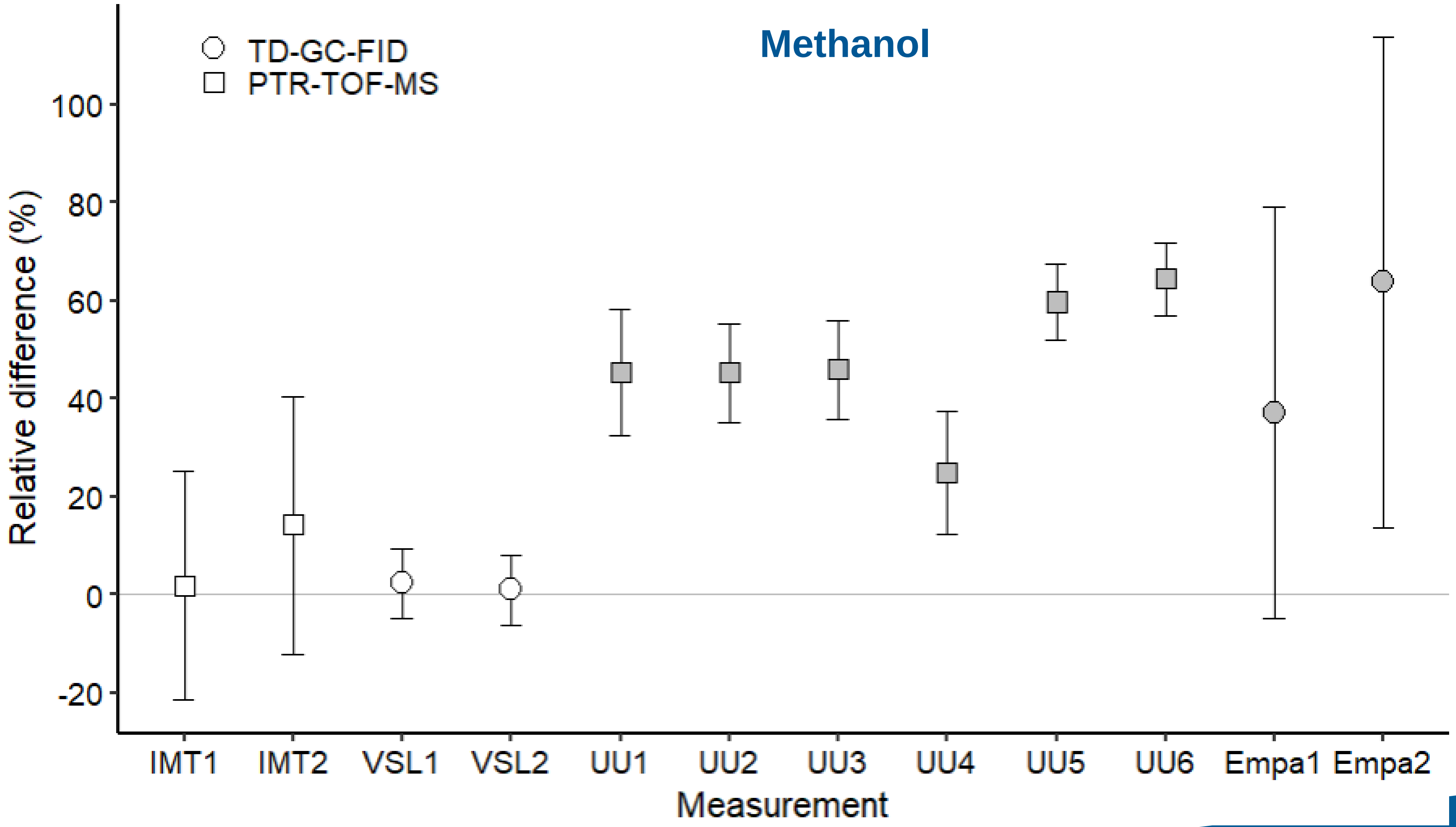


- Dilution of RGM using METAS dilution system (IMT, UU, Empa) and VSL dilution system (VSL)
- WS1 amount fractions ca.10 nmol mol^{-1} (IMT, VSL) and < 5 nmol mol^{-1} (UU, Empa)

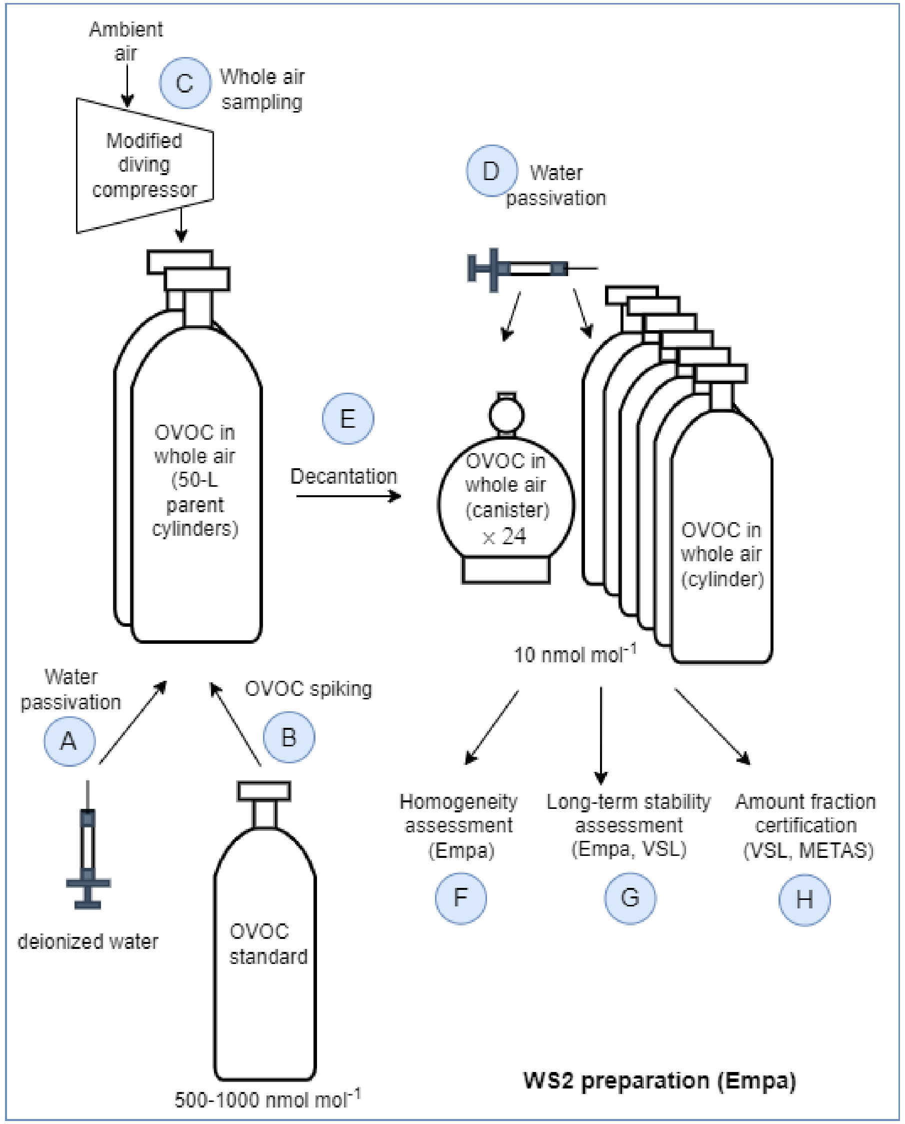
Dilution of reference gas mixtures (WS1) - results



Dilution of reference gas mixtures (WS1) - results



Certified spiked whole air samples (WS2) - methodology



Volume (L)	Material	Treatment	Pressure (bar) approx.	Quantity
10	aluminium	Experis	105	4
3.6	stainless steel	SilcoNert 2000	99	2
15	stainless steel	Silonite	4.1	2
6	stainless steel	Silonite	3.5	10
6	stainless steel	Siltek	4.1	12

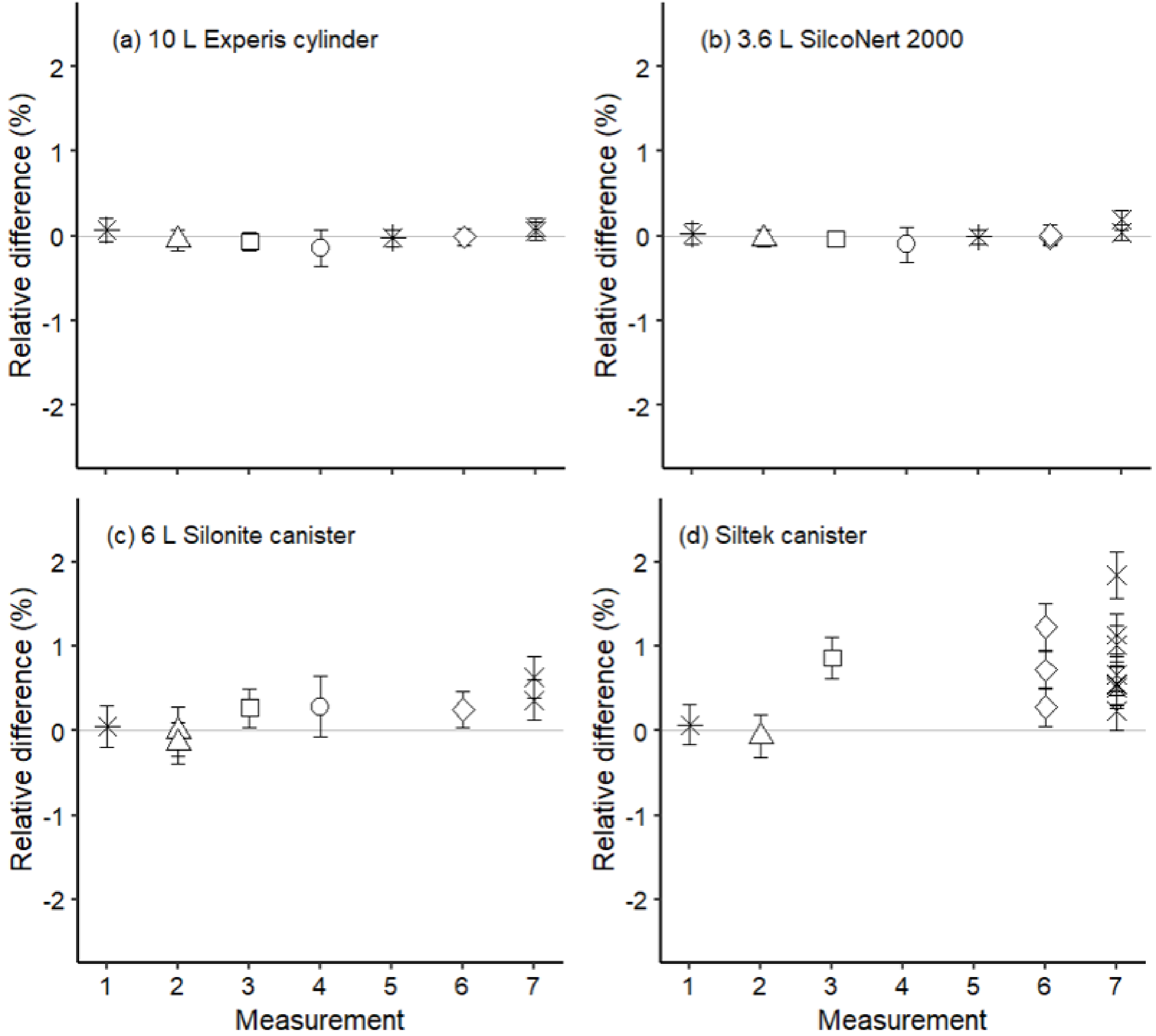
Certified spiked whole air samples (WS2) – results

Acetone

Measurements performed between

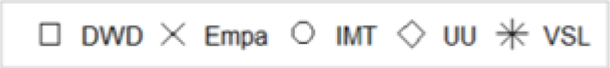
July 2021 (1) and November 2022 (7)

Jul. 2021 (1), Feb. 2022 (2), Mar. 2022 (3), Jun. 2022 (4), Aug. 2022 (5), Sep. 2022 (6), Nov. 2022 (7)



Certified spiked whole air samples (WS2) – results

Methyl ethyl ketone (MEK)



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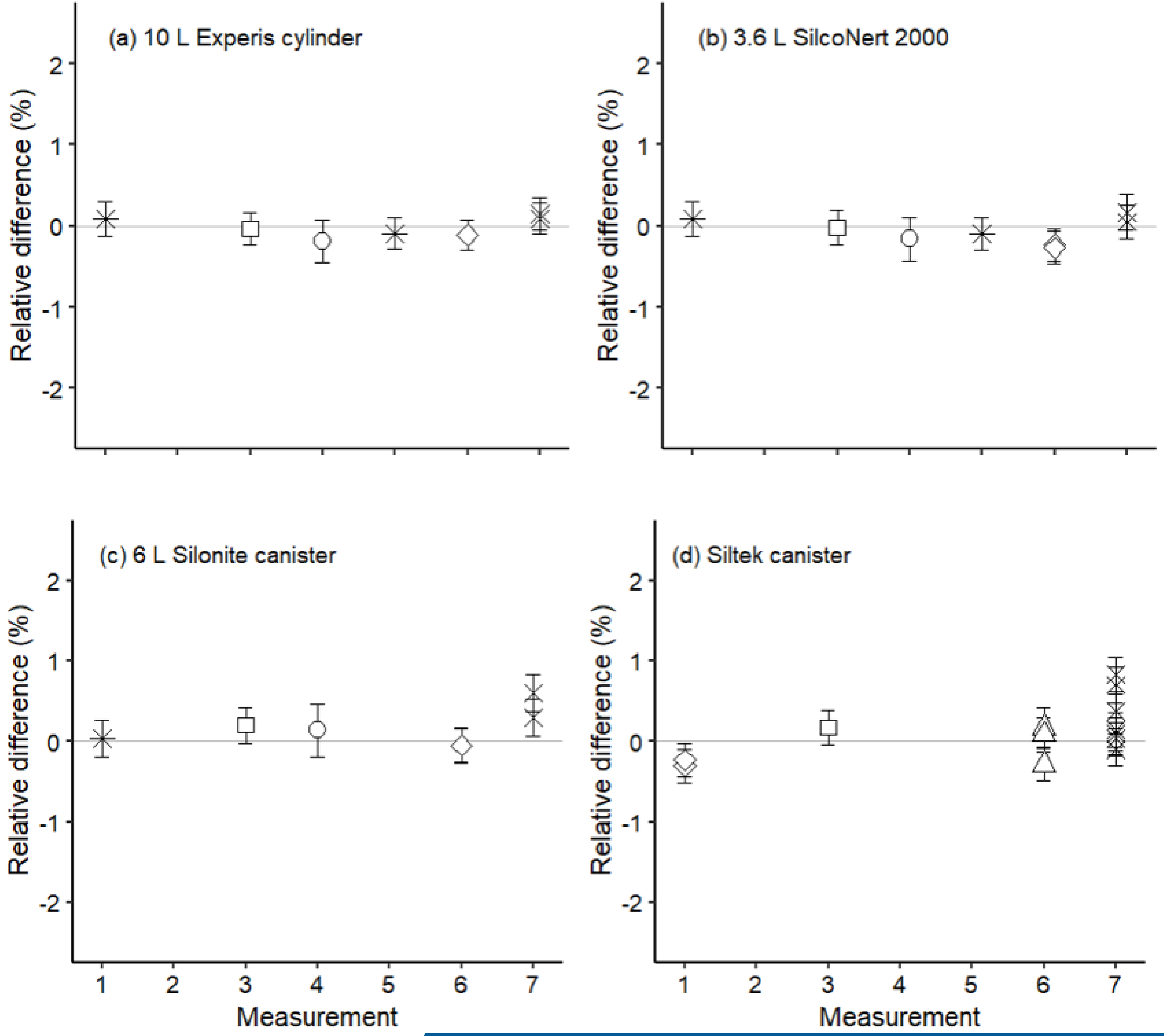
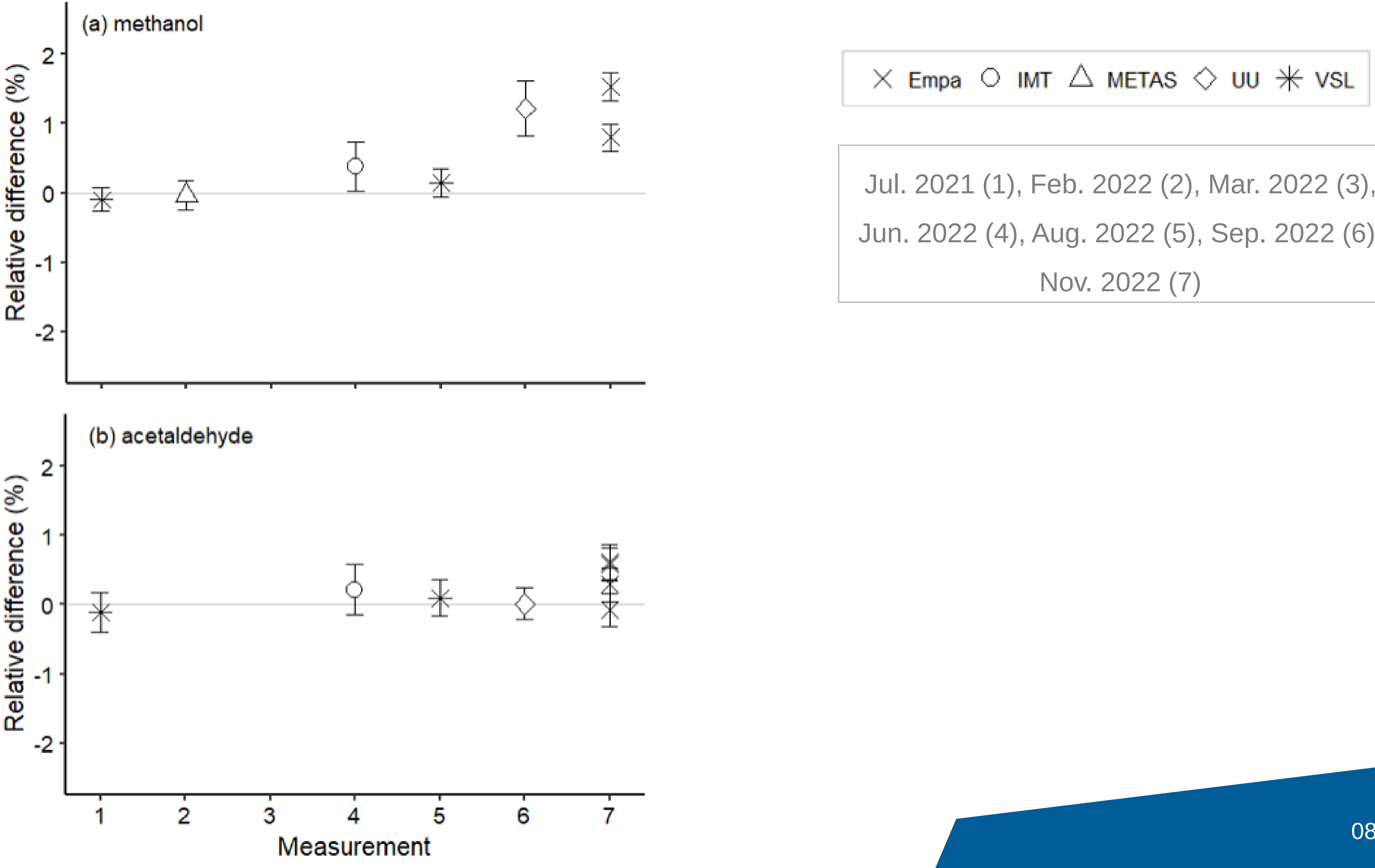


Certified spiked whole air samples (WS2) – results



Jul. 2021 (1), Feb. 2022 (2), Mar. 2022 (3), Jun. 2022 (4), Aug. 2022 (5), Sep. 2022 (6), Nov. 2022 (7)

OVOC SI-traceable working standards – outlook

SI-traceable RGMs at amount fractions around 100 nmol mol^{-1} and temporal stability ≥ 14 months:

- ✓ Acetone
- ✓ Methacrolein
- ✓ MEK
- ✓ MVK
- ✓ Ethanol
- ✗ Methanol
- ✗ Acetaldehyde

(Methanol, Acetaldehyde:) Further research on suitable cylinder materials and optimal preparation and analytical procedure (e.g., cylinder wall passivation) to minimise surface adsorption and reaction effects (→ temporal instability)

OVOC SI-traceable working standards – outlook

To generate working standards at ambient level amount fractions (i.e., 4–10 nmol mol^{-1}) using the described RGMs (WS1) and to ensure their SI-traceability, the use of a traceable dilution system is crucial.

- [x] Acetone
- [ ] Methacrolein
- [x] MEK
- [ ] MVK
- [ ] Ethanol
- [x] Methanol
- [ ] Acetaldehyde

Expanded uncertainty U (k = 2) < 10 %

(for acetone and MEK, U < 4 %)

OVOC SI-traceable working standards – outlook

Certified spiked whole air samples in high-pressure cylinders at amount fractions around 10 nmol mol^{-1} with temporal stability of 12–14 months:

- ☑ Acetone
- ❑ Methacrolein
- ☑ MEK
- ❑ MVK
- ❑ Ethanol
- ❑ Methanol
- ☑ Acetaldehyde

Further research on matrix gas effects on the analytical systems, and effects of water passivation and vessel wall effects on the stability of OVOC working standards based on whole air samples. Differences due to vessel material or to other factors (e.g., pressure and volume difference)?

Matrix gas similar to the ambient air analysed

Expanded uncertainty U (k = 2) < 5 %

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MetClim VOC

https://www.metclimvoc.eu

METAS
Ihre Referenz.

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Institut für Metrologie METAS

EMPIR EURAMET

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