Dynamic formaldehyde standards and their analysis by FTIR – methods and uncertainties

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Workshop on VOCs,
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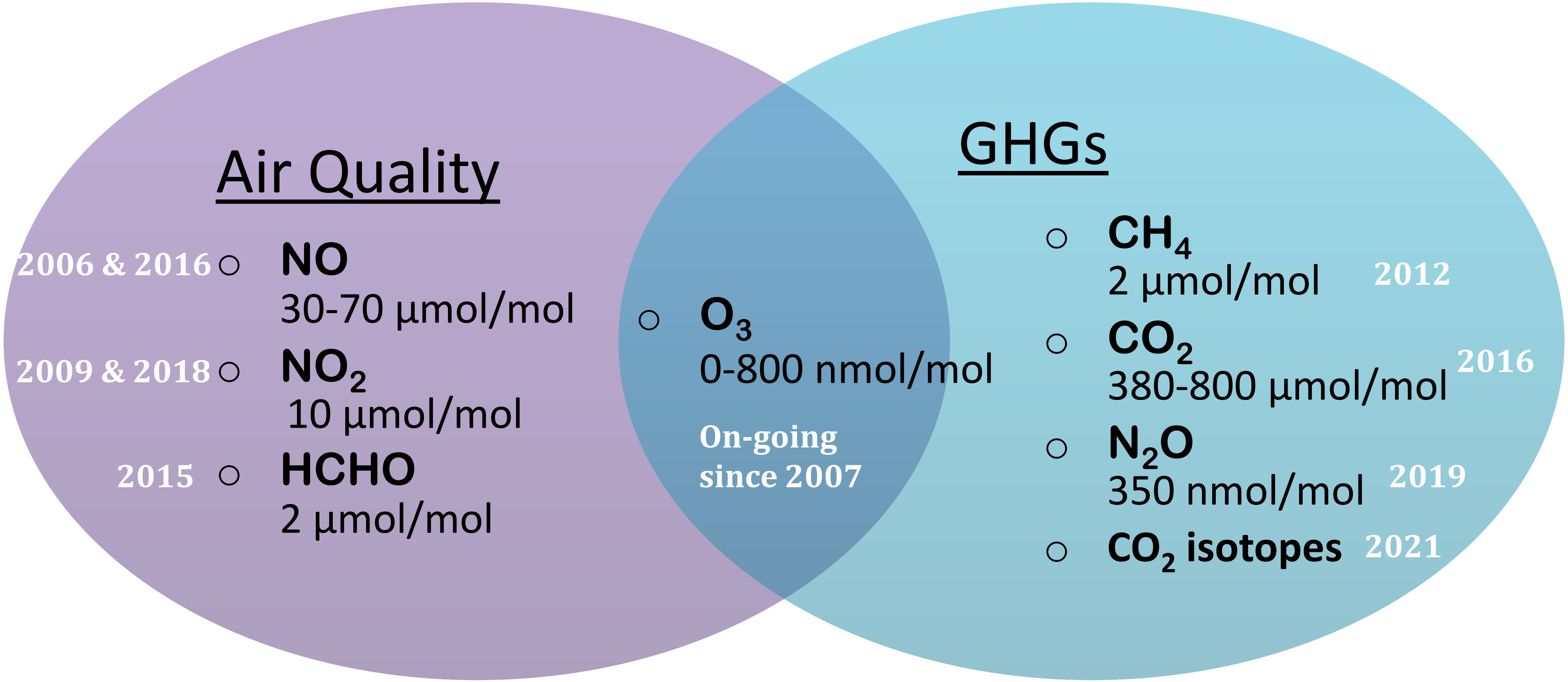
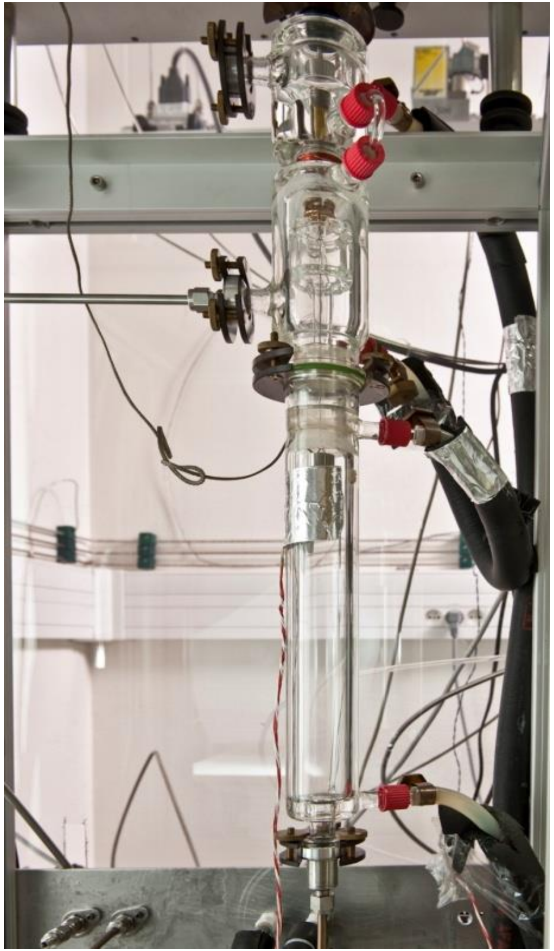
Outline

- Services of the BIPM Chemistry Department
- Dynamic generation of formaldehyde in nitrogen standards
- Analysis by FTIR
- Uncertainties
- Key Comparison CCQM-K90

BIPM Chemistry Department / Coordinating CCQM key comparisons for Air Quality and GreenHouse Gas standards



Dynamic generation of formaldehyde in nitrogen standards



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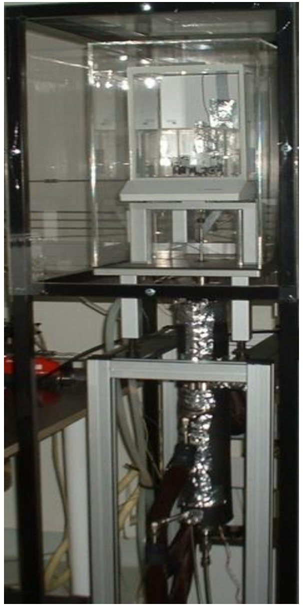
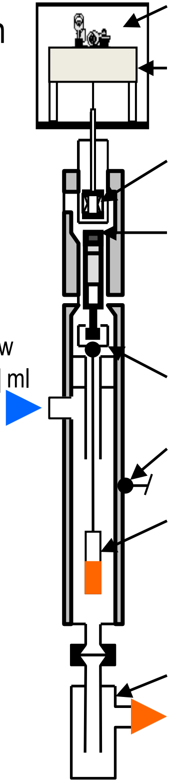
Magnetic Suspension Balance





Magnetic **S**uspension **B**alance:

- Mass load 20 g
- Resolution 2 µg
- Stability over 3 days ~ 0.5 µg

Measurement of the **mass** of the permeation tube emitting the analyte

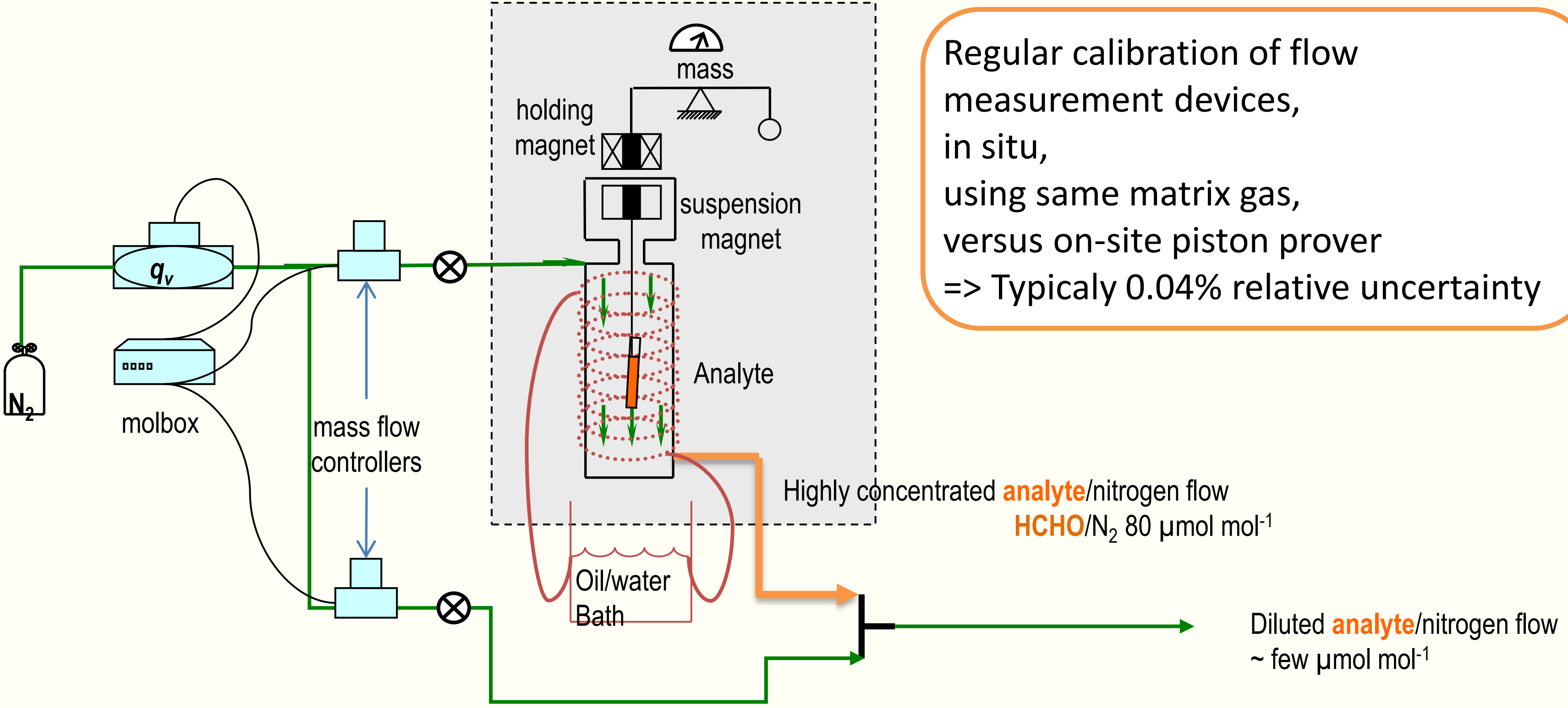
Deduction of the **permeation rate q_m / (ng min^{-1})**
= mass loss per unit of time

$$q_m = \frac{dm}{dt}$$

And the amount of substance fraction

$$x_A = \frac{q_m V_m}{q_v M_A}$$

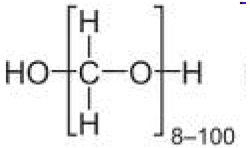
Flow control & measurement



Regular calibration of flow measurement devices,
in situ,
using same matrix gas,
versus on-site piston prover
=> Typicaly 0.04% relative uncertainty

Generation of formaldehyde in nitrogen mixtures

Permeation tube at 110°C

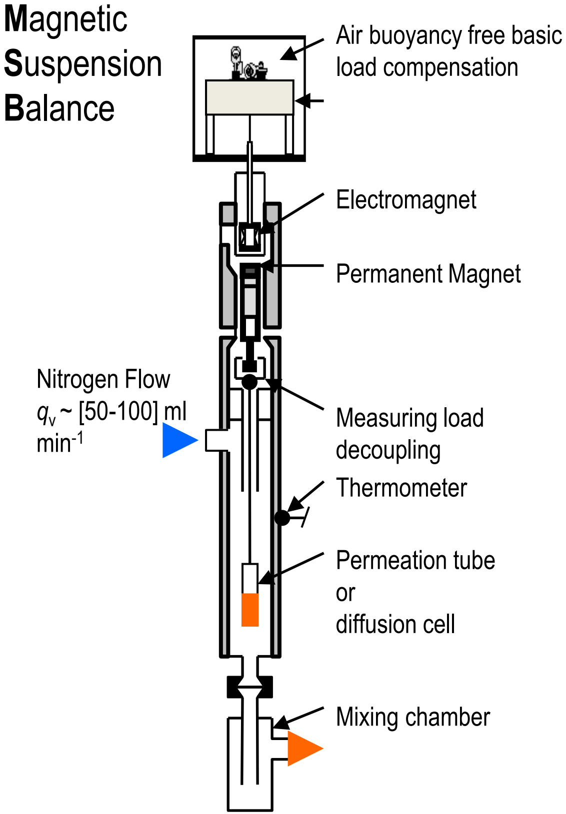


Paraformaldehyde

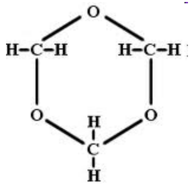
+ correction for co-emitted water

$$x_{\mathrm{HCHO}} = \frac{q_m V_m}{q_v M_{\mathrm{HCHO}}} - \frac{M_{\mathrm{H_2O}}}{M_{\mathrm{HCHO}}} x_{\mathrm{H_2O}}$$

Water content measured by CRDS with/without permeation tube in the chamber. Typically 0.5%



Diffusion cell at 20°C



Trioxane

+ converter at 200°C

$$x_{\mathrm{HCHO}} = \frac{3 q_m V_m}{q_v M_{(\mathrm{HCHO})_3}} \beta_{\mathrm{conv}}$$

Conversion factor measured by FTIR with/without converter. 100% conversion with 0.1% uncertainty.

Purity analysis by FTIR

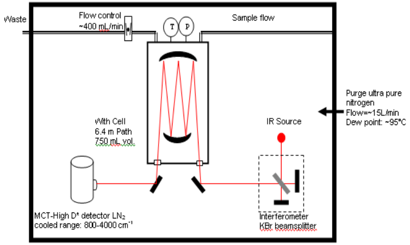
Fourier Transformed InfraRed spectrometer to quantify (infrared actives) impurities
Calibration either with gravimetric standards or using molecular parameters

Database of spectroscopic parameters
(**HITRAN** or PNNL or NIST library)

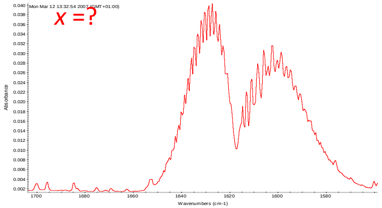
21 2290.645159 2.450E-25 7.574E-02.0877.1204 3245.3348 .75 .000000 56 18 Q 3 455 2 2 1
22 2290.662655 6.192E-24 4.750E-02.0670.0772 2073.5014 .78 .000000 25 5 R 42 455 2 2 1
23 2290.666003 9.230E-24 4.987E-02.0713.0966 1495.8581 .76 .000000 24 4 P 21e455 2 2 1
. . .

Synthetic calibration – uncertainty driven by database
5-10 %

FTIR

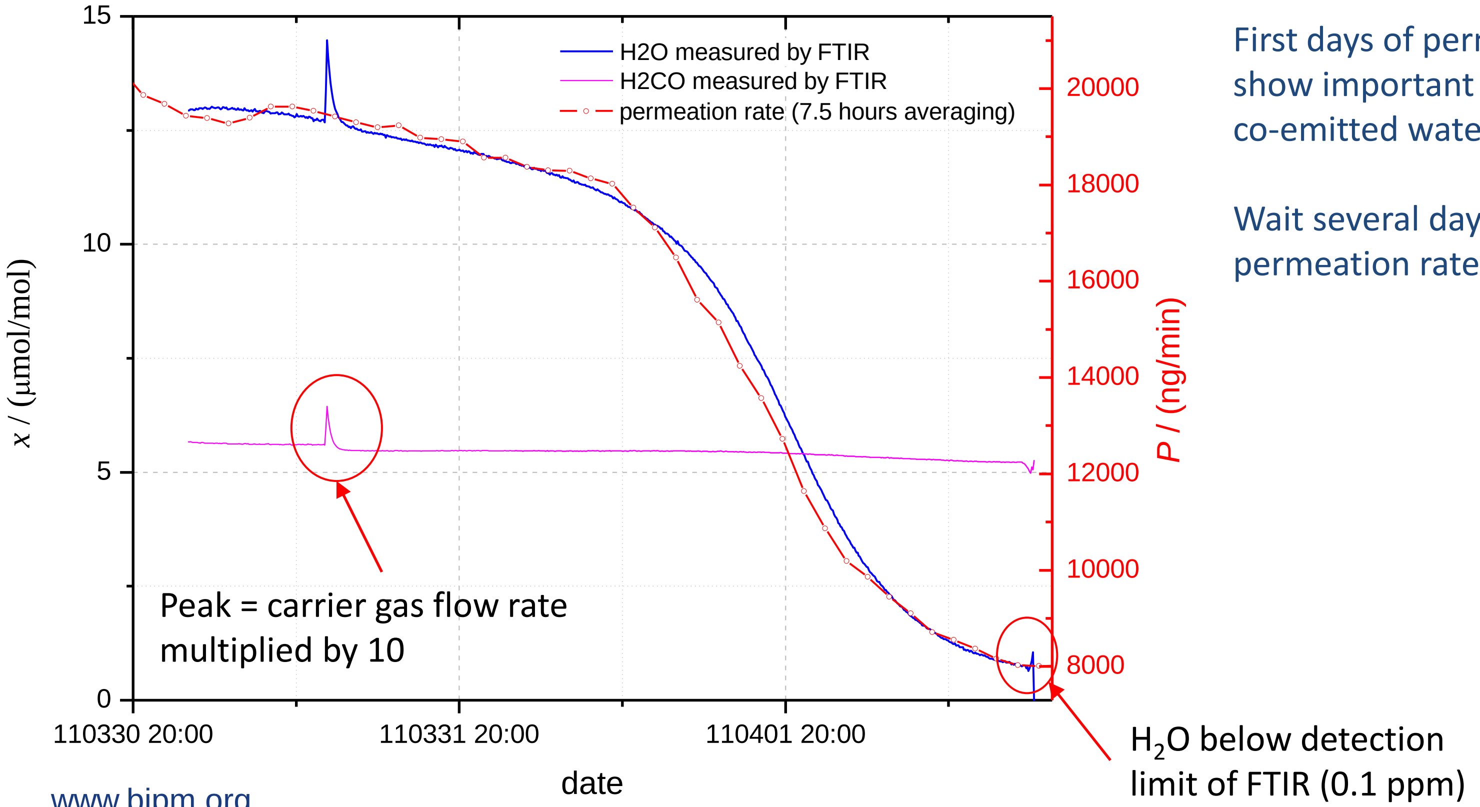


Measured spectrum



Gas standard calibration –
uncertainty driven by gravimetry
< 1%

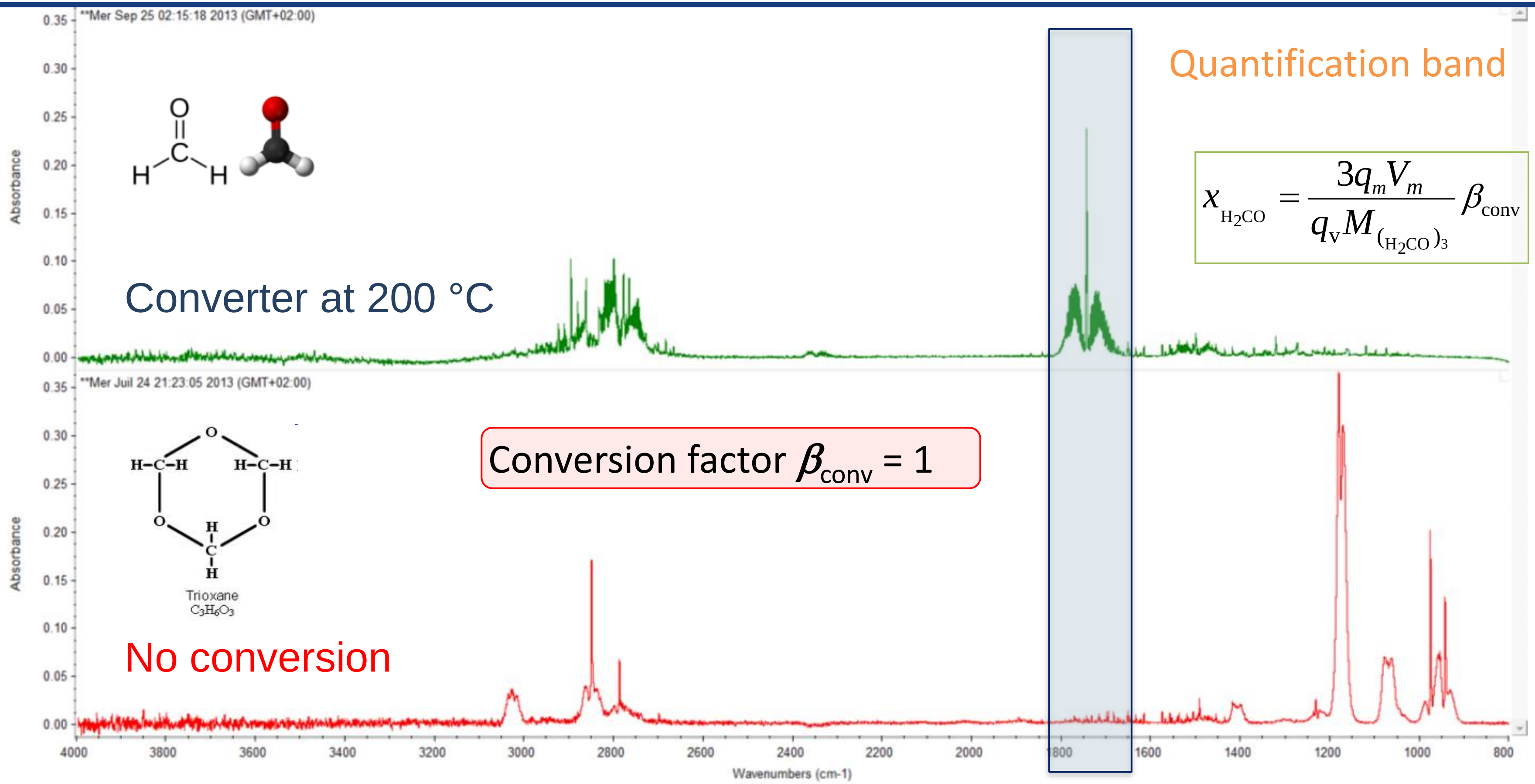
Paraformaldehyde purity versus age of the permeation tube



First days of permeation from tubes show important amount of co-emitted water

Wait several days to get “stable” permeation rate (mass loss)

Trioxane to Formaldehyde conversion factor **by FTIR**



Quantification band

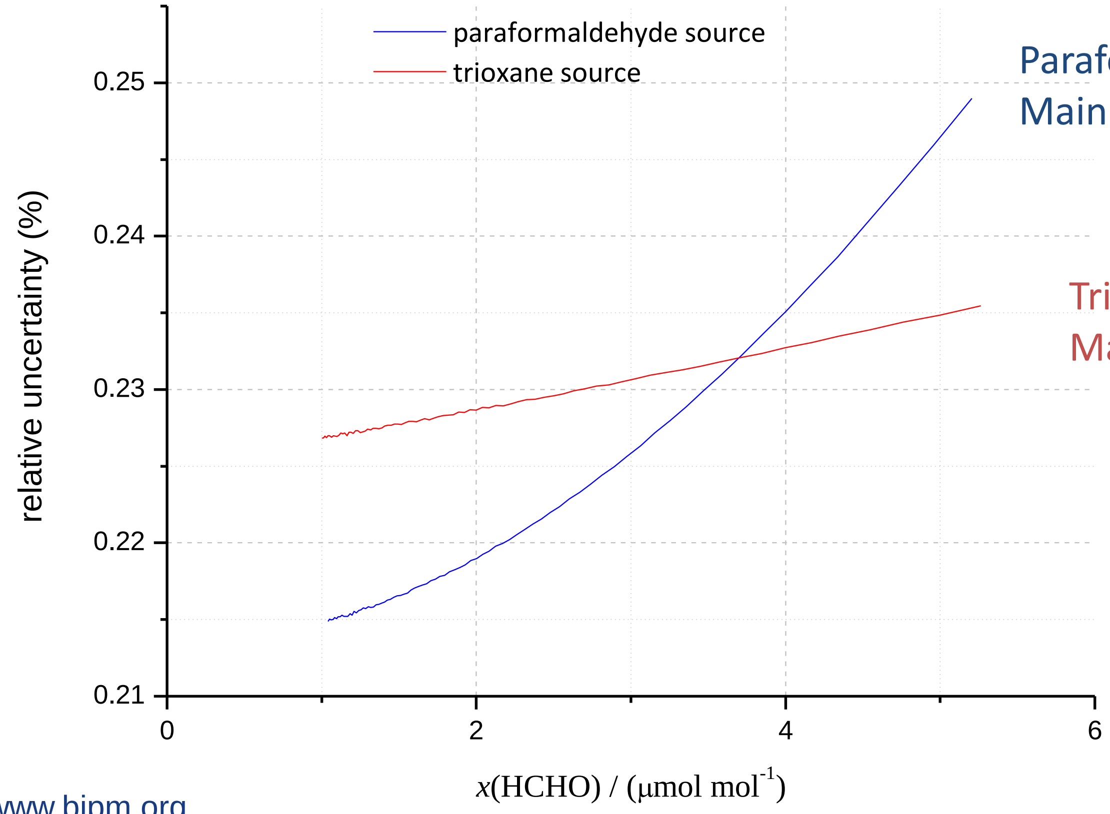
$$x_{H_2CO} = \frac{3 q_m V_m}{q_V M_{(H_2CO)_3}} \beta_{conv}$$

Converter at 200 °C

Conversion factor β_{conv} = 1

No conversion

Uncertainty of dynamic calibration gases



Paraformaldehyde source at 110°C
Main uncertainty from H_2O impurity

Trioxane source at 20°C
Main uncertainty from residual trioxane

Uncertainty of dynamic calibration gases

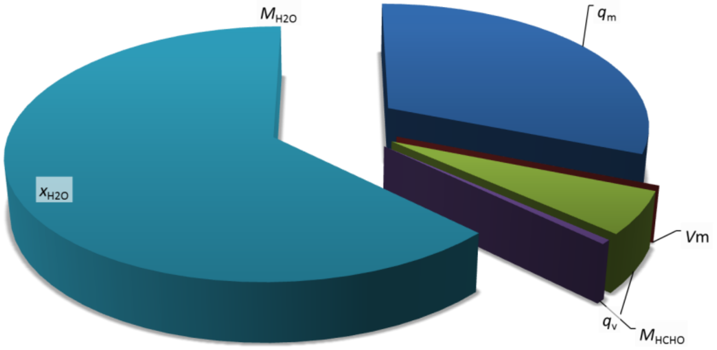
HCHO from paraformaldehyde

$$x_{\mathrm{HCHO}} = \frac{q_m V_m}{q_v M_{\mathrm{HCHO}}} - \frac{M_{\mathrm{H_2O}}}{M_{\mathrm{HCHO}}} x_{\mathrm{H_2O}}$$

Quantity	Value	unit	Standard relative uncertainty
q_m	7000.00	ng min^{-1}	1.21×10^{-3}
V_m	22.4037	L mol^{-1}	1.52×10^{-5}
q_v	2.5	L min^{-1}	5.12×10^{-4}
M_{HCHO}	30.026	g mol^{-1}	6.66×10^{-5}
x_{H2O}	12.00	nmol mol^{-1}	5.00×10^{-1}
M_{H2O}	18.053	g mol^{-1}	2.77×10^{-5}

- $q_m(t)$ modelled by second order polynomial during analysis period
- q_V measured by Molbloc calibrated before measurements,
- x_{H2O} measured by CRDS calibrated by NPL, with/without permeation tube in chamber

Quantity	Value	Standard Uncertainty
x(HCHO)	2.082 µmol mol^{-1}	0.005 µmol mol^{-1}



Uncertainty of dynamic calibration gases

HCHO from trioxane

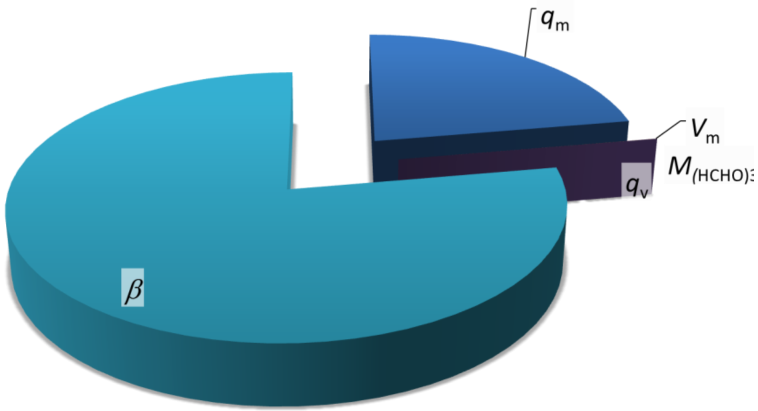
$$x_{\mathrm{HCHO}} = \frac{3q_m V_m}{q_v M_{(\mathrm{HCHO})_3}} \beta_{\mathrm{conv}}$$

Quantity	Value	unit	Standard relative uncertainty
q_m	6700.00	ng min^{-1}	9.1×10^{-4}
V_m	22.4037	L mol^{-1}	1.52×10^{-5}
q_v	2.5	L min^{-1}	5.12×10^{-4}
$M_{(\mathrm{HCHO})3}$	90.078	g mol^{-1}	2.22×10^{-5}
β	1		1.70×10^{-3}

Quantity	Value	Standard Uncertainty
x(HCHO)	2.000 µmol mol^{-1}	0.005 µmol mol^{-1}

- $q_\mathrm{m}(t)$ modelled by second order polynomial during analysis period
- q_V measured by Molbloc calibrated before measurements,
- β measured by FTIR previously calibrated with trioxane,

with/without trioxane-formaldehyde converter



CCQM-K90 (2015)

Purpose: Demonstrate the degree of equivalence of national formaldehyde in nitrogen gas standards in support of air quality regulations **(CCQM-K90, HCHO in N_2)**

Set of transfer standards value assigned by BIPM

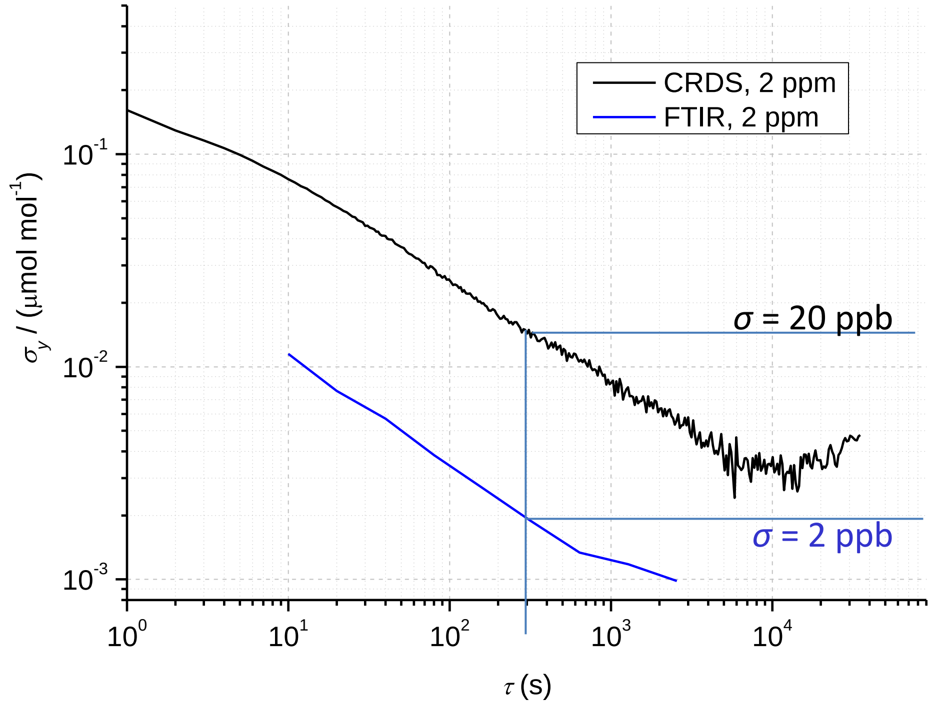
List of participants

- NPL National Physical Laboratory
- NIST
- KRISS
- LNE
- NMIJ
- ВНИИМ
- VSL Dutch Metrology Institute
- NIM

- *Dynamic generation of HCHO/N_2 by permeation & continuous weighing with a **Magnetic Suspension Balance***
- *Analysis made by Cavity **R**ing-**D**own **S**pectroscopy and **FTIR***

Analytical instruments used for comparisons

Allan deviation on HCHO at 2 µmol mol^{-1}

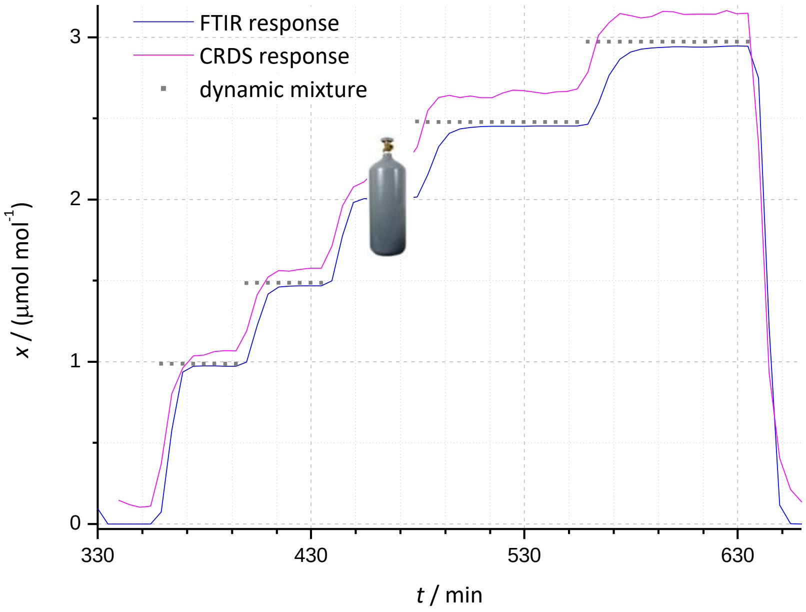


Uncertainty component for analytical instruments

- Allan deviation evaluated before each series
- Standard uncertainty σ_{allan} **(300 s)**
- FTIR typically 2 nmol mol^{-1}
- CRDS typically 4 nmol mol^{-1}

Measurement process to value assign a cylinder

One cylinder value assignement sequence (~ 300 min)



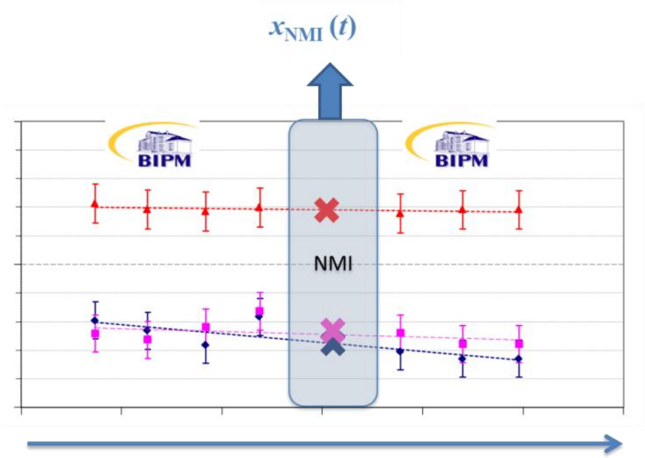
Each cylinder value assigned with 4 points calibration method

- Bracketing with 4 dynamic values
- Generalised Least-Square fit (B_Least)
- Correlation between dynamic mixtures

Transfer standards in CCQM-K90 (2015)

Total of 14 standards = 8 transfer + 6 control

- **Content :** HCHO in N_2, nominal mole fraction 2 µmol mol^{-1}.
- **Source :** commercial producer of specialty calibration gases
- **Type** : high pressure cylinders, ~ 115 bars



Stability study in protocol

- **principle:** measure x(HCHO) during more than 3 months before/after shipment to calculate x at the date of measurements by participants.

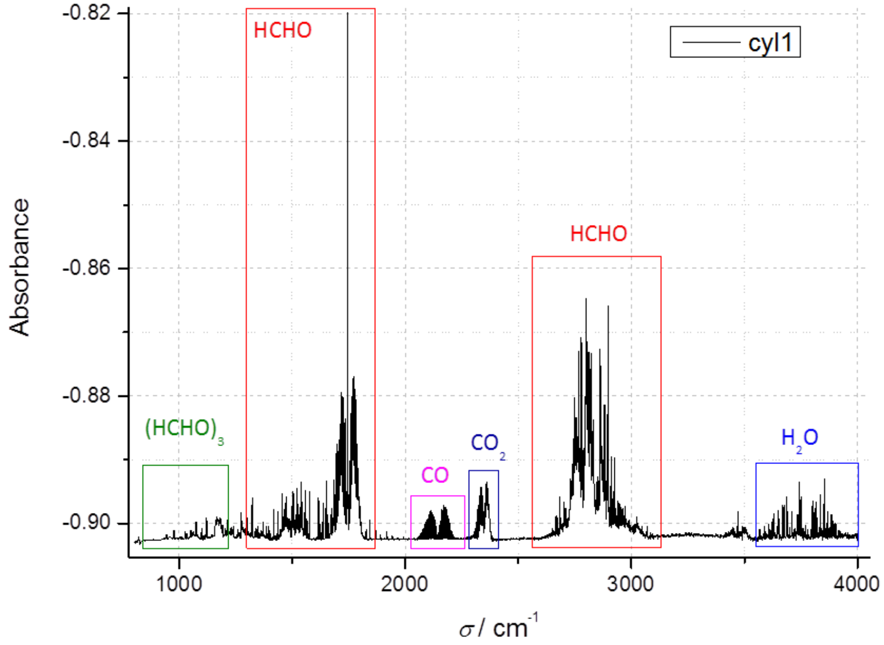
Transfer standards purity analysis

FTIR analysis for HCHO and impurities

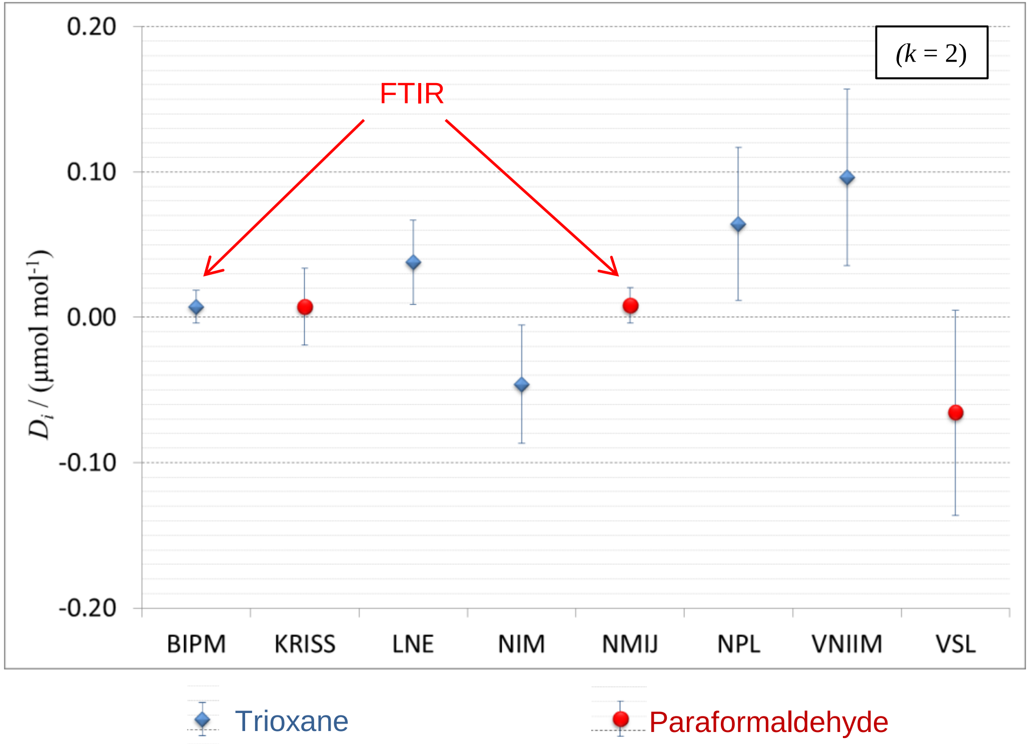
- **When :** during each series of measurements.
- **How :** Thermo Nicolet Nexus with 45m path length gas cell + IMACC software suits for quantification
- **Calibration** (for impurities)

synthetic calibration using HITRAN 2012 parameters for CO, H_2O, CO_2

calibration with dynamic standards for $(HCHO)_3$



CCQM-K90 (2015) results



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KEY COMPARISON

CCQM-K90, formaldehyde in nitrogen, 2 µmol mol^{-1} Final report

Joële Viallon[1], Edgar Flores[1], Faraz Idrees[1], Philippe Moussay[1], Robert Ian Wielgosz[1], D Kim[2], Y D Kim[2], S Lee[2], S Persijn[3], L A Konopelko[4] +Show full author list

Metrologia, Volume 54, Technical Supplement

+Article information

Abstract

The CCQM-K90 comparison is designed to evaluate the level of comparability of national metrology institutes (NMI) or designated institutes (DI) measurement capabilities for formaldehyde in nitrogen at a nominal mole fraction of 2 µmol mol^{-1}.

The comparison was organised by the BIPM using a suite of gas mixtures prepared by a producer of specialty calibration gases. The BIPM assigned the formaldehyde mole fraction in the mixtures by comparison with primary mixtures generated dynamically by permeation coupled with continuous weighing in a magnetic suspension balance. The BIPM developed two dynamic sources of formaldehyde in nitrogen that provide two independent values of the formaldehyde mole fraction: the first one based on diffusion of trioxane

https://iopscience.iop.org/article/10.1088/0026-1394/54/1A/08029

Conclusions

- Generation of dynamic standards is a valuable solution, providing a good control/measurement of the mass loss, flow rate, and **purity**
- Dynamic standards of HCHO in nitrogen 2 µmol mol^{-1} can be generated either from **paraformaldehyde** or **trioxane**, with **0.2%** relative standard uncertainty
- FTIR demonstrated good repeatability + useful tool to monitor the efficiency of dynamic sources
- Standards in high pressure cylinders showed loss of HCHO lower than expected, ~ 2 nmol mol^{-1} $month^{-1}$, **predictable** with **linear behavior**

Thank you.

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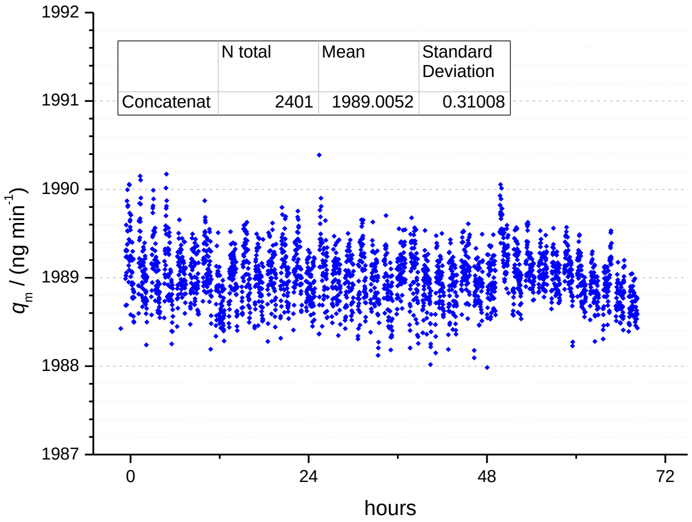
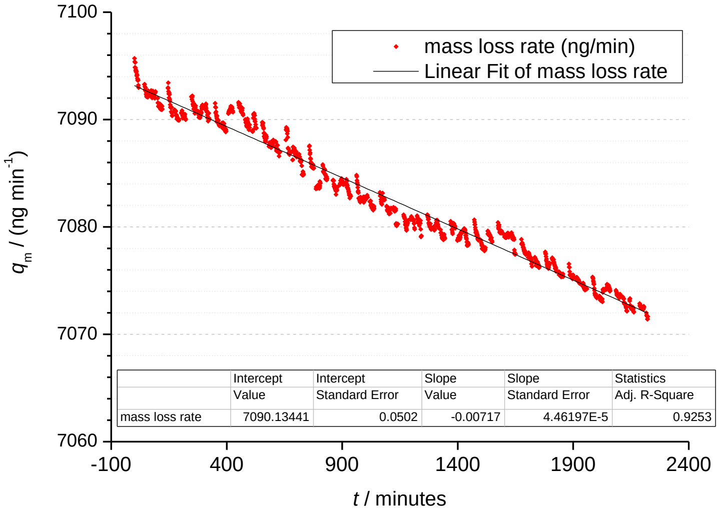
Mass loss rate analysis

q_m is almost never constant, even at constant temperature control





Trioxane diffusion source at 5°C

Low values 1900 ng min^{-1}

Slow drift

Source duration > 1 year

Paraformaldehyde permeation source at 110°C

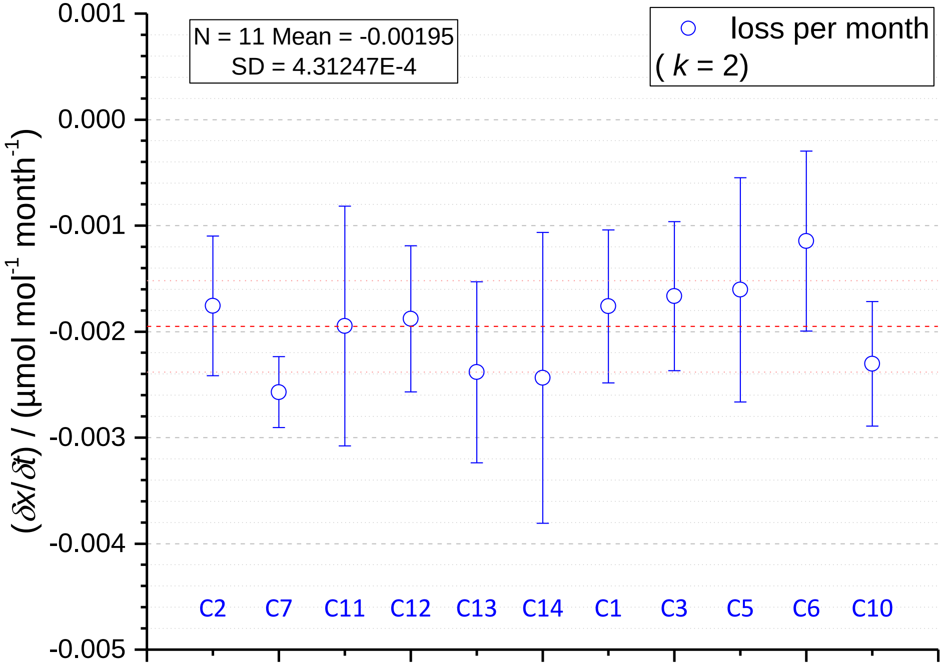
Large values 7000 ng min^{-1}

Faster drift

Source duration < 4 months

Transfer standard stability

HCHO loss in all standards



Loss deduced from regression line

- Loss = regression slope
- Calculated on 11 mixtures (1 empty, 2 away)
- Very consistent values
- Average -0.002 μmol mol^{-1} month^{-1}