Gas standards for climate and air quality monitoring

R.I. Wielgosz

Bureau International des Poids et Mesures

Outline

- Introduction to Air Quality and Greenhouse Gas Monitoring
- Methods for Gas Standard preparation and verification
- Static Gravimetric Methods (CH_4 and NO)
- Dynamic Methods (NO_2 and HCHO)
- Spectroscopic Methods including isotopologues (O_3 and FTIR)
- Manometric Methods (CO_2 and O_3)

Air Quality and Greenhouse Gases

Air Quality

Greenhouse Gases

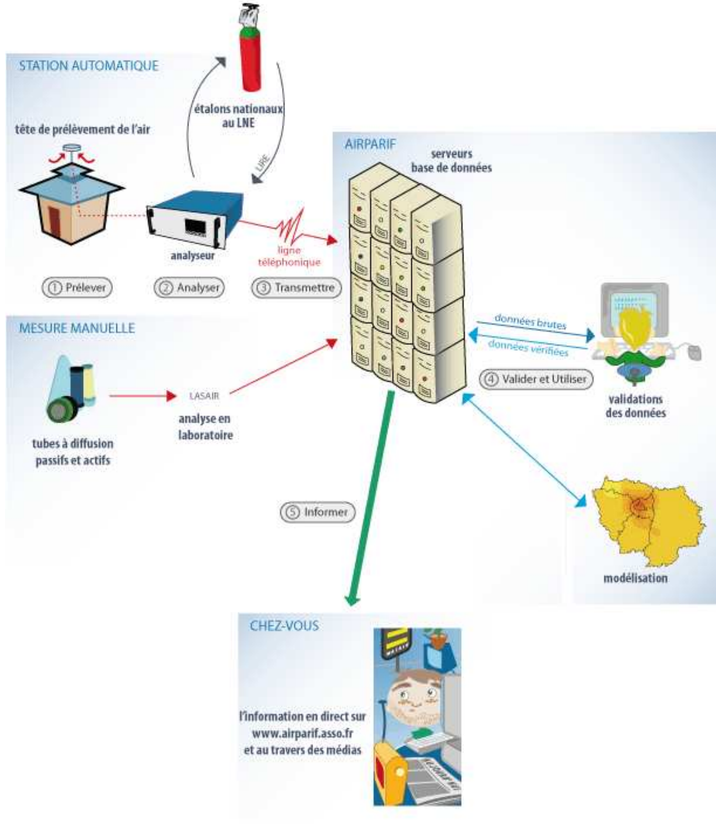
Pollutant	*Concentration*	*Averaging period*
Ozone	60 nmol/mol	Maximum daily 8 hour mean
Sulphur dioxide (SO_2)	120 nmol/mol	1 hour
	45 nmol/mol	24 hours
Nitrogen dioxide (NO_2)	100 nmol/mol	1 hour
	20 nmol/mol	1 year
Carbon monoxide (CO)	8 µmol/mol	Maximum daily 8 hour mean
Benzene	1.5 nmol/mol	1 year
Fine particles (PM2.5)	25 $\mu g/m^3$	1 year
PM10	50 $\mu g/m^3$	24 hours
	40 $\mu g/m^3$	1 year
Lead (Pb)	0.5 $\mu g/m^3$	1 year

GAS	**Recent tropospheric concentration**
Carbon dioxide (CO_2)	392.6 µmol/mol
Methane (CH_4)	1874 nmol/mol
Nitrous oxide (N_2O)	324 nmol/mol
Tropospheric ozone (O_3)	34 nmol/mol
Halocarbons	(0.003 to 0.5) nmol/mol

(Limit value concentrations)

Emission gases not included in list

Air Quality Monitoring Networks



GCOS
GLOBAL CLIMATE OBSERVING SYSTEM

The Essential Climate Variables

ECVs are either specific variables or groups of closely-related variables:

Atmospheric	**Surface:**	Air temperature, wind speed and direction, water vapour, pressure, precipitation, surface radiation budget
	Upper-air:	Temperature, wind speed and direction, water vapour, cloud properties, earth radiation budget (including solar irradiance)
	Composition:	Carbon dioxide, methane, and other long-lived greenhouse gases, ozone and aerosol, supported by their precursors
Oceanic	**Surface:**	Sea-surface temperature, sea-surface salinity, sea level, sea state, sea ice, surface current, ocean colour, carbon dioxide partial pressure, ocean acidity, phytoplankton
	Sub-surface:	Temperature, salinity, current, nutrients, carbon dioxide partial pressure, ocean acidity, oxygen, tracers
Terrestrial	River discharge, water use, groundwater, lakes, snow cover, glaciers and ice caps, ice sheets, permafrost, albedo, land cover (including vegetation type), fraction of absorbed photosynthetically active radiation, leaf area index, above-ground biomass, soil carbon, fire disturbance, soil moisture	

For details see GCOS, 2010: Implementation plan for the global observing system for climate in support of the UNFCCC (2010 update) GCOS Rep. 138, 186 pp.

WMO UNESCO IOC UNEP ICSU International Council for Science

ECMWF

Deutscher Wetterdienst DWD
Wetter und Klima aus einer Hand

Table 1: Essential Climate Variables that are both currently feasible for global implementation and have a high impact on UNFCCC requirements

Domain	Essential Climate Variables	
Atmospheric (over land, sea and ice)	**Surface:**[8]	Air temperature, Wind speed and direction, Water vapour, Pressure, Precipitation, Surface radiation budget.
	Upper-air:[9]	Temperature, Wind speed and direction, Water vapour, Cloud properties, Earth radiation budget (including solar irradiance).
	Composition:	Carbon dioxide, Methane, and other long-lived greenhouse gases[10], Ozone and Aerosol, supported by their precursors[11]
Oceanic	**Surface:**[12]	Sea-surface temperature, Sea-surface salinity, Sea level, Sea state, Sea ice, Surface current, Ocean colour, Carbon dioxide partial pressure, Ocean acidity, Phytoplankton.
	Sub-surface:	Temperature, Salinity, Current, Nutrients, Carbon dioxide partial pressure, Ocean acidity, Oxygen, Tracers.
Terrestrial	River discharge, Water use, Groundwater, Lakes, Snow cover, Glaciers and ice caps, Ice sheets, Permafrost, Albedo, Land cover (including vegetation type), Fraction of absorbed photosynthetically active radiation (FAPAR), Leaf area index (LAI), Above-ground biomass, Soil carbon, Fire disturbance, Soil moisture.	

8 Including measurements at standardized, but globally varying heights in close proximity to the surface.

9 Up to the stratopause.

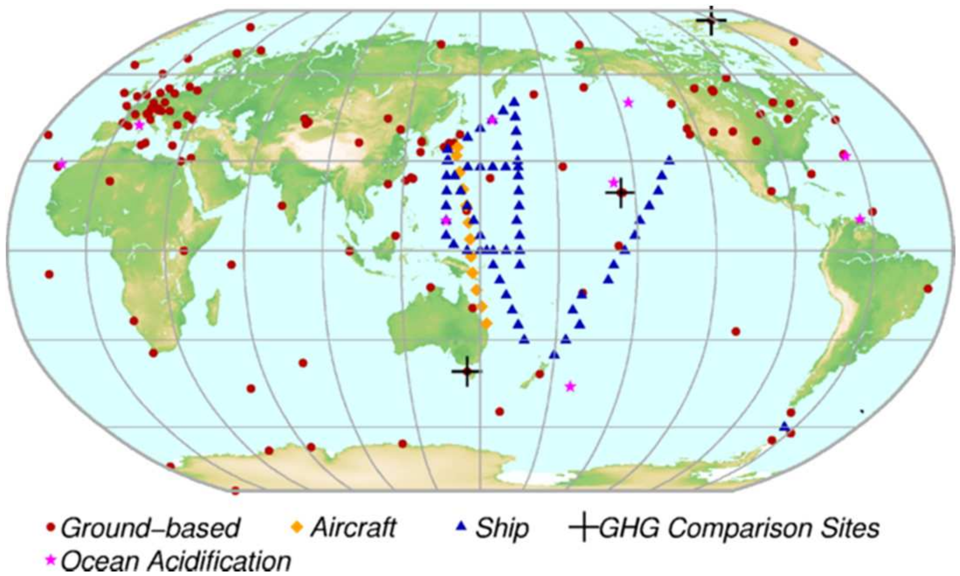
10 Including N_2O, CFCs, HCFCs, HFCs, SF_6 and PFCs.

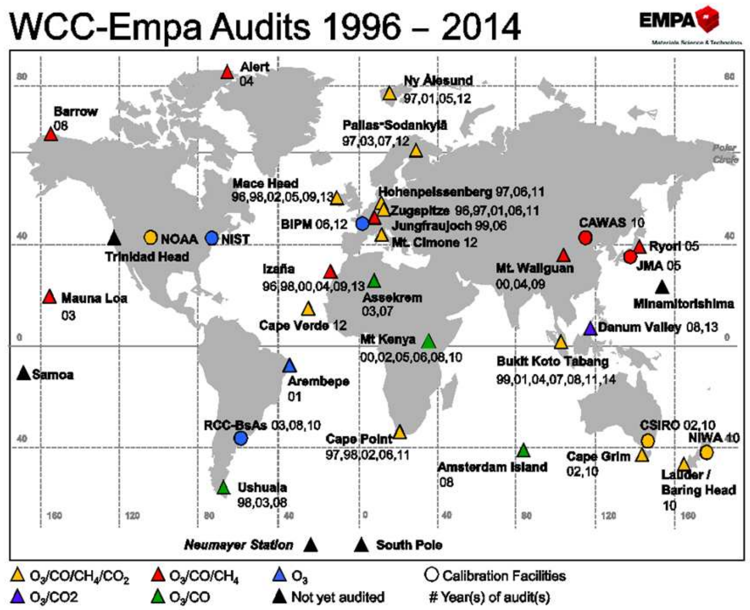
11 In particular NO_2, SO_2, HCHO and CO.

12 Including measurements within the surface mixed layer, usually within the upper 15 m.

Greenhouse Gases: A Global View

WMO GAW GHG Network





The network consists of 141, 123 and 49 fixed stations on the ground for CO_2, CH_4 and N_2O respectively. About 13%, 13% and 18% of the stations perform both discrete air sampling in "flasks" and continuous measurements of CO_2, CH_4 and N_2O, respectively.

Data Quality Objectives for GHGs

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO_2	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm	250 – 520 ppm
CH_4	± 2 ppb	± 5 ppb	1700 – 2100 ppb	300 – 2600 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	20 -500 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb	260 – 370 ppb
SF_6	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt	1.1 – 9.8 ppt
H_2	± 2 ppb	± 5 ppb	450 – 600 ppb	140 – 1200 ppb
$\delta^{13}C$-CO_2	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB	
$\delta^{18}O$-CO_2	± 0.05‰	± 0.1‰	-2 to +2‰ vs. VPDB	
$\Delta^{14}C$-CO_2	± 0.5‰	± 3‰	0-70‰	
$\Delta^{14}C$-CH_4	± 0.5‰		50-350‰	
$\Delta^{14}C$-CO	± 2 molecules cm^{-3}		0-25 molecules cm^{-3}	
$\delta^{13}C$-CH_4	± 0.02‰	± 0.2‰		
δD-CH_4	± 1‰	± 5‰		
O_2/N_2	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

Reviewed at GGMT-2013

Target uncertainties for GHG primary standards

Component	Nominal Mole fraction	Primary Standard: target standard uncertainty
CO_2	400 µmol/mol	0.025 µmol/mol
CH_4	2000 nmol/mol	0.5 nmol/mol
N_2O	330 nmol/mol	0.025 nmol/mol

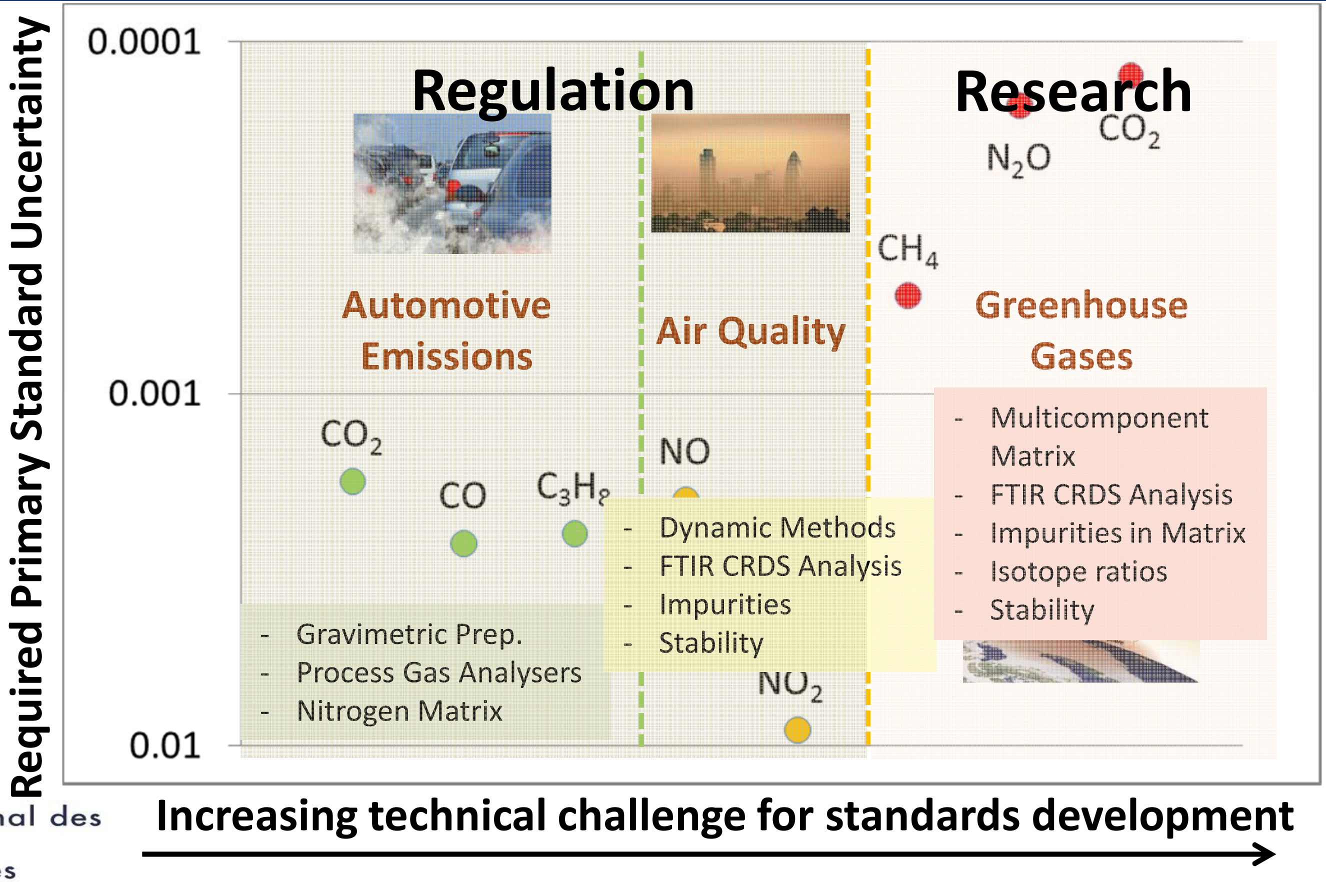
Based on primary standard contributing to less than 5% of measurement uncertainty for monitoring, based on most stringent data compatibility requirements

This means relative standard uncertainties:

< 0.007 % (for CO_2 and N_2O) and

< 0.025 % (for CH_4)

Gas Standards in support of Regulation and Research



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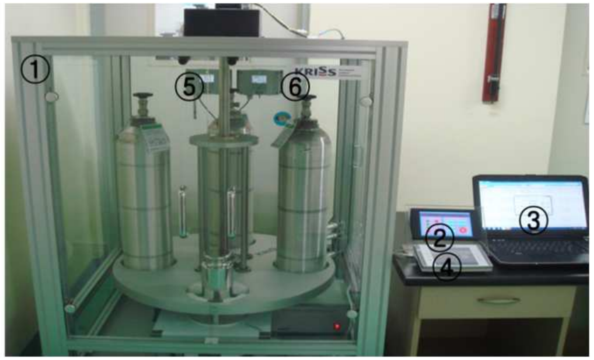
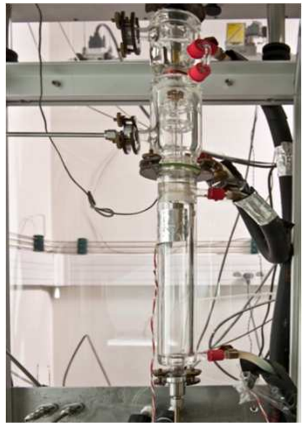
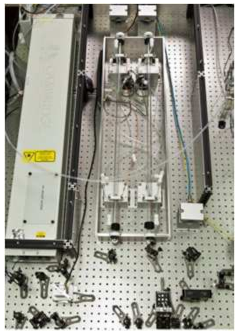
Methods for Gas Standard Preparation and Value Assignment

Static Gravimetry

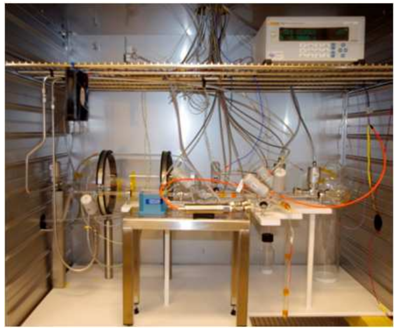


Dynamic Methods





Spectroscopic Methods



Manometric Methods

Gas Standards: International documentary standards

- ISO TC158 Gas Analysis
- ISO 6142 : Gas Analysis – Preparation of calibration gas mixtures – Gravimetric method
- ISO 6143 : Gas Analysis – Comparison methods for determining and checking the composition of calibration gas mixtures

Preparation of Gas Standards (Static)

- Purity Analysis of Gases; Impurity Analysis; purity = 1- Σx_i
  GC(FID, TCD, ECD, AED, USD, DID, SCD, MSD)
  Dedicated Analyzer(H_2, O_2, Ar, N_2, CH_4, CO, CO_2, SO_2, NO_x, H_2O, THC, CFCs, PFCs)
  FTIR, Gas MS
- Gravimetry, Micro-gravimetry;
  Top-loading Electronic Balance
  (10 kg/1mg, 15 kg/1 mg, 23 kg/1 mg , 1 kg/0.01 mg, 22 g/1 µg)
  Substitution Method, Capillary Method

Calculation of Mixture Composition (ISO 6142)

$$x_i = \frac{\sum_{A=1}^{P}\left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^{n} x_{i,A} \cdot M_i}\right)}{\sum_{A=1}^{P}\left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A} \cdot M_i}\right)}$$

x_i is the mole fraction of component i in the resulting mixture

P is the total number of the parent gases

n is the total number of the parent gases

m_A is the mass of the parent gas A measured by weighing

M_i is the molar mass of component I

$x_{i,A}$ is the mole fraction i in the parent gas A

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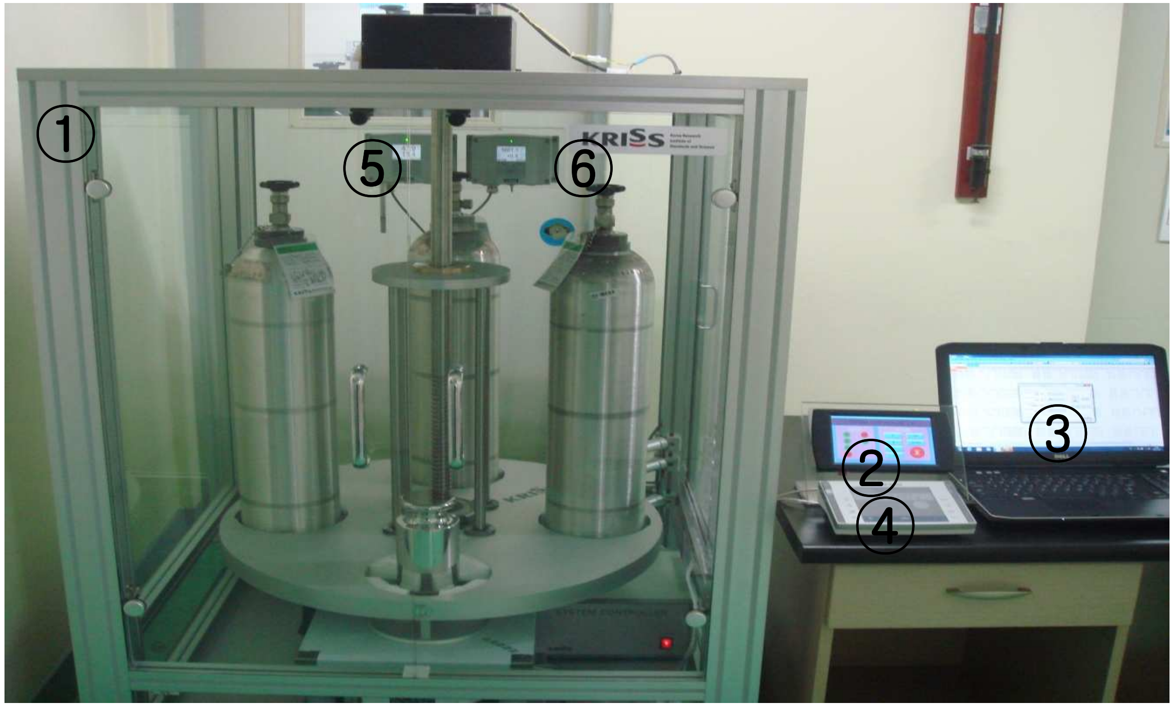
Automatic Gas Cylinder Weighing System (KRISS)



① Draft shiled

② Manual controller
(LCD touch screen)

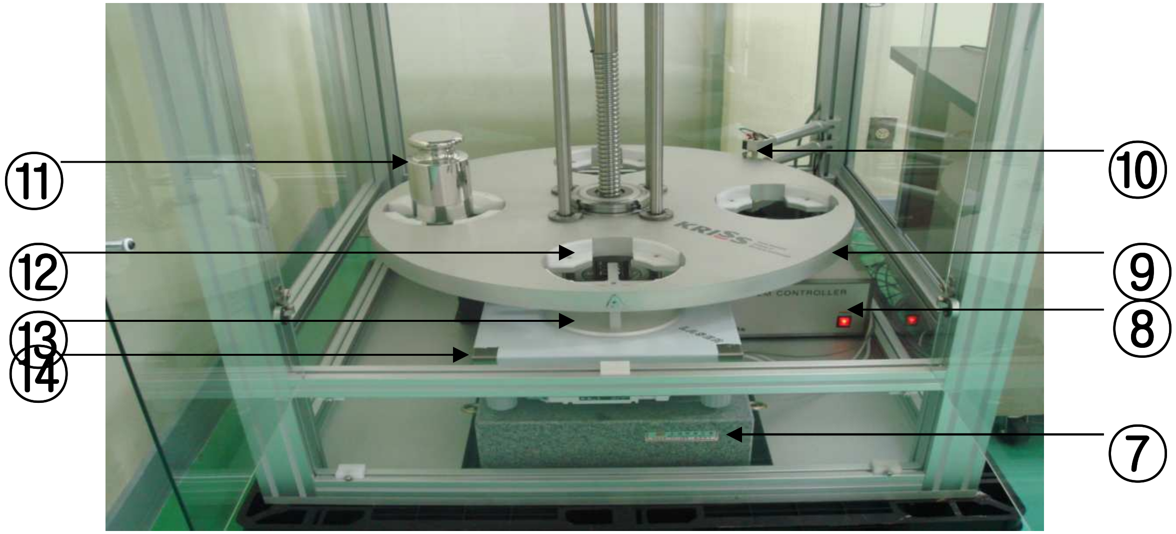
③ Computer

④ Balance display(LCD)

⑤ Humidity & Temp.
Transmitter

⑥ Barometer

Automatic Gas Cylinder Weighing System (KRISS)



⑦ Stone plate

⑧ System controller

⑨ Rotation plate

⑩ Upper & limit sensor

⑪ Mass(D)

⑫ Cylinder position(A, B, C)

⑬ Cylinder support

⑭ Balance

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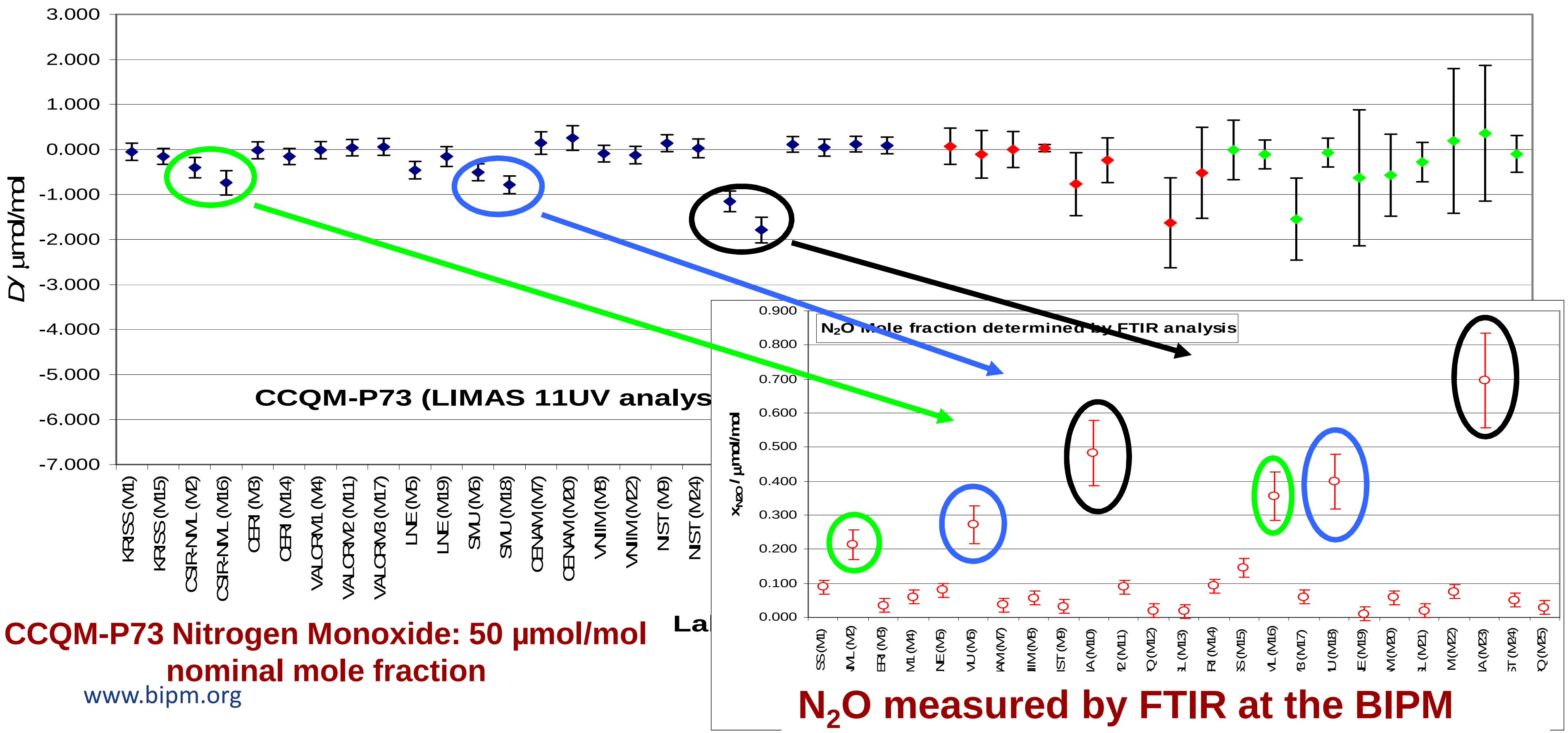
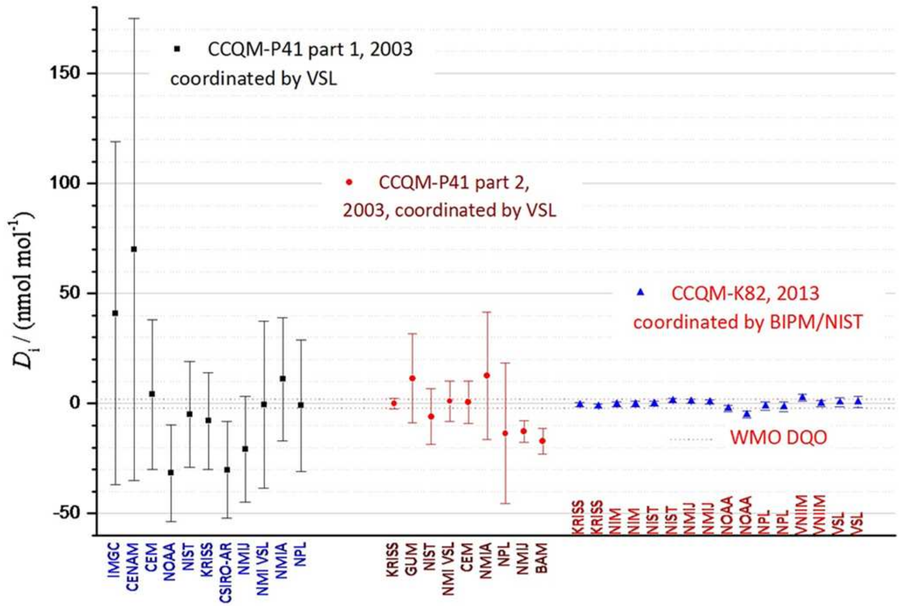
Equivalence of standards produced by Static Gravimetry (NO in N_2)



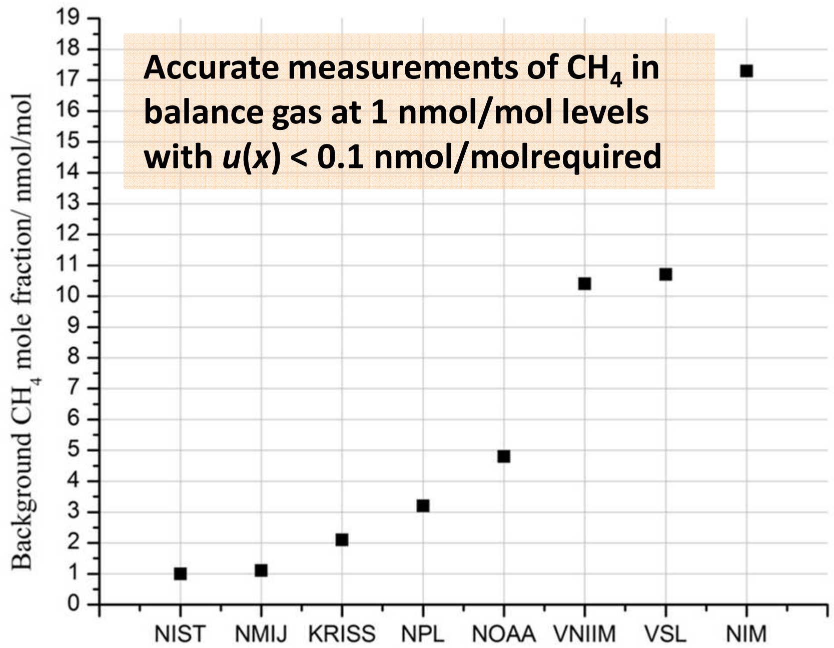
CCQM-P73 Nitrogen Monoxide: 50 µmol/mol nominal mole fraction

www.bipm.org

Equivalence of standards produced by Static Gravimetry (CH_4 in Air)

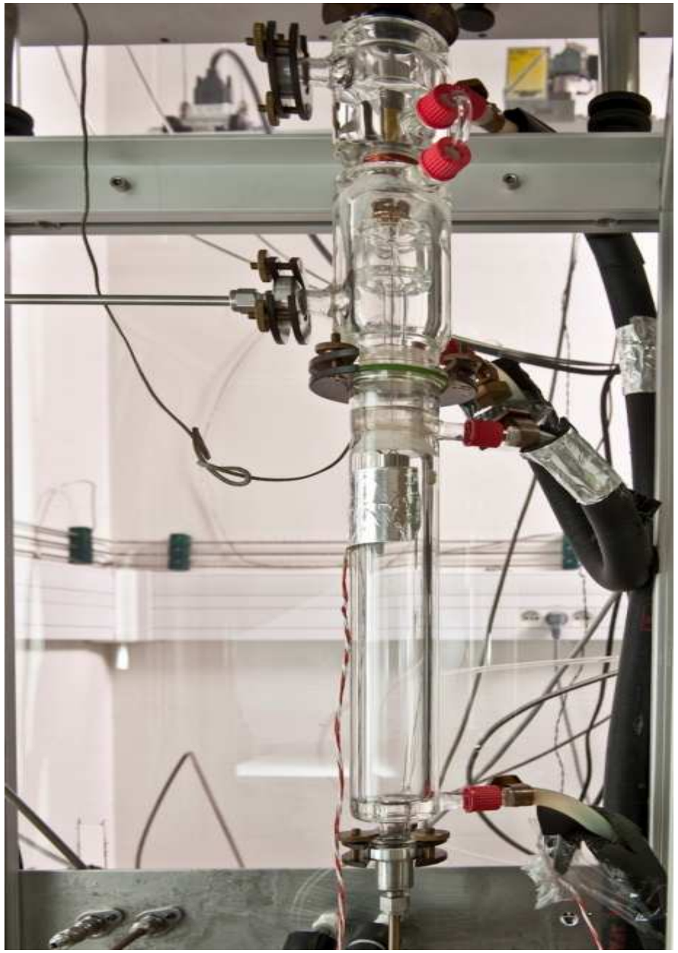


Methane in air nominal mole fraction 2000 nmol/mol



Trace CH_4 mole fractions in balance gas as reported by participating laboratories in CCQM-K82

Dynamic gas standard generation



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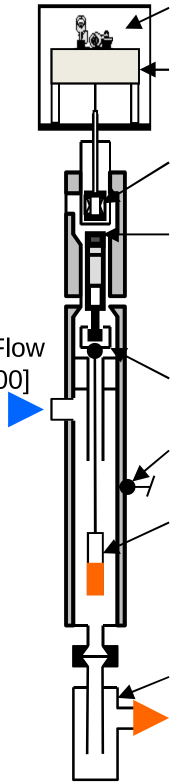
Magnetic Suspension Balance

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

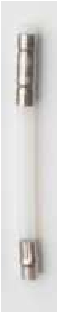
Deduction of the **permeation rate q_m / (ng min^{-1})**
= mass loss per unit of time

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

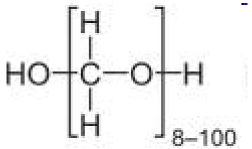
And the amount of substance fraction

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

Generation of formaldehyde in nitrogen mixtures



Permeation tube at 110°C



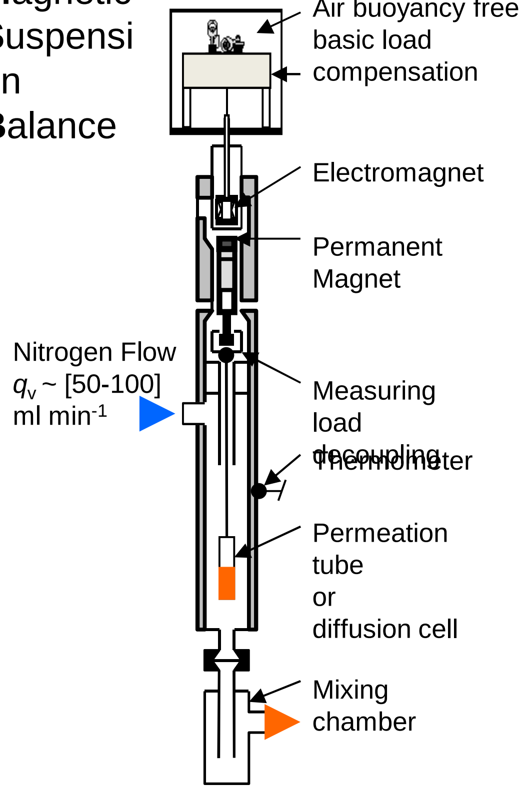
Paraformaldehyde

+ correction for co-emitted water

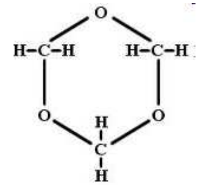
$$x_{\mathrm{HCHO}} = \frac{q_m V_m}{q_v M_{\mathrm{HCHO}}} - \frac{M_{\mathrm{H_2O}}}{M_{\mathrm{HCHO}}} x_{\mathrm{H_2O}}$$

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

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



Diffusion cell at 20°C



Trioxane

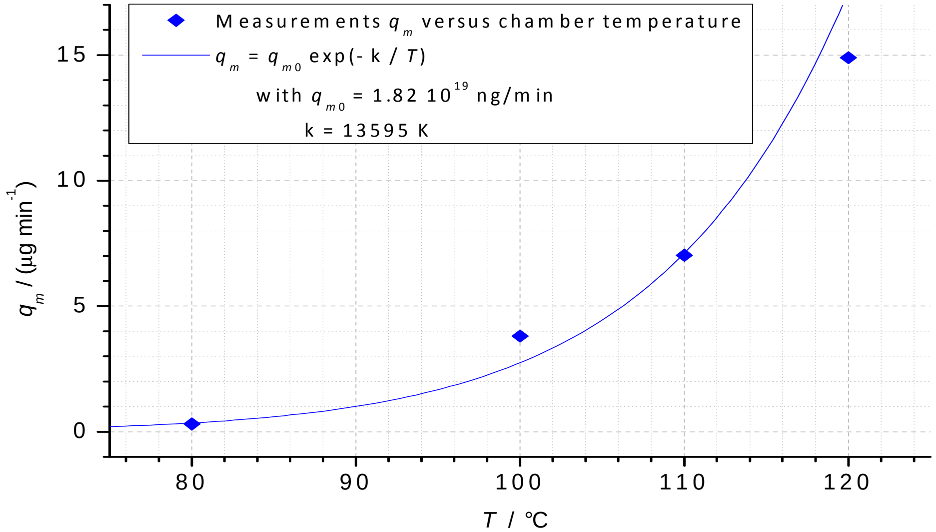
+ converter at 200°C

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

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

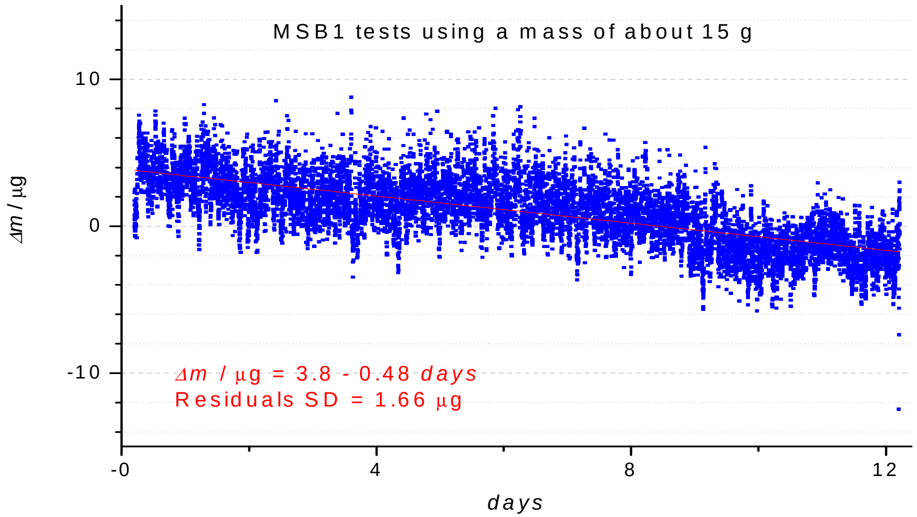
Choice of source temperature

Chamber temperature to be defined to reach the target analyte concentration….



Mass loss rate vs. gas chamber temperature study (paraformaldehyde source)

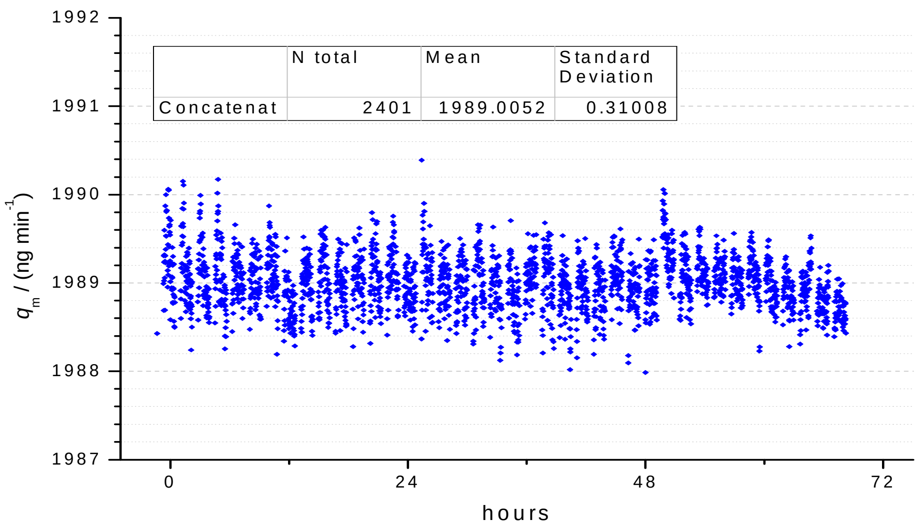
… and maintained within fixed limits

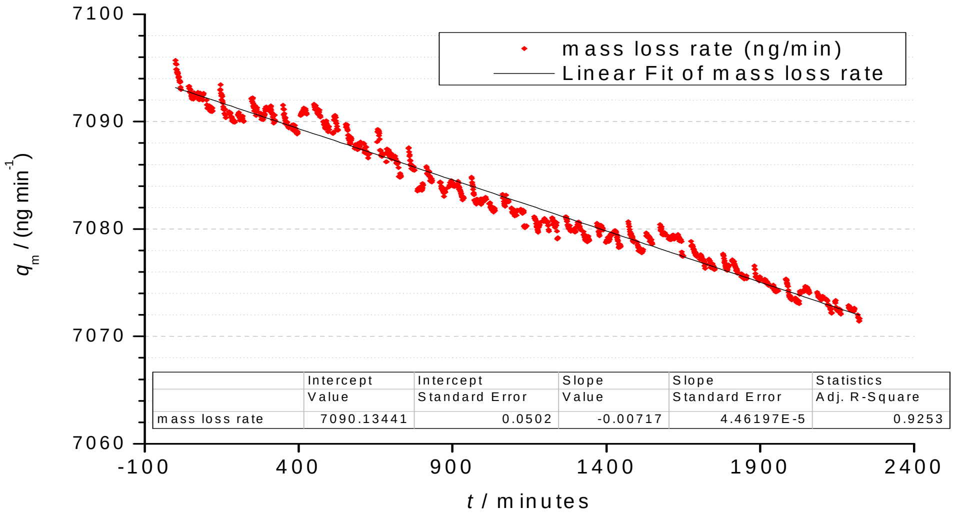


Target noise RSD < 3 µg
With temperature noise < 0.01 K

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

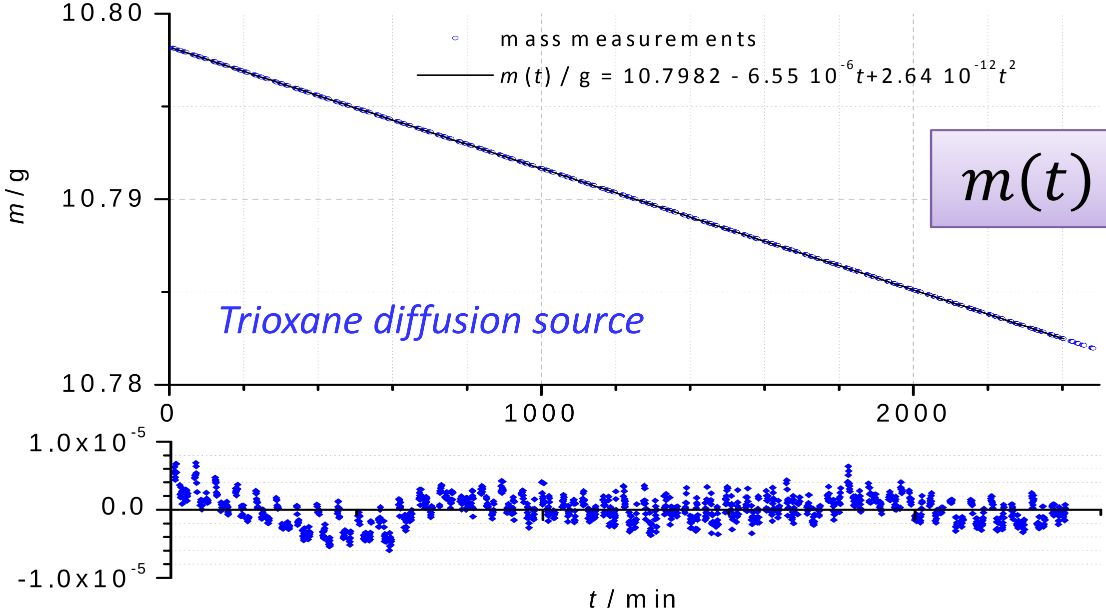
Large values 7000 ng min^{-1}

Faster drift

Source duration < 4 months

Choice of statistical analysis

Polynomial fit of mass continuous measurements during a typical analysis period

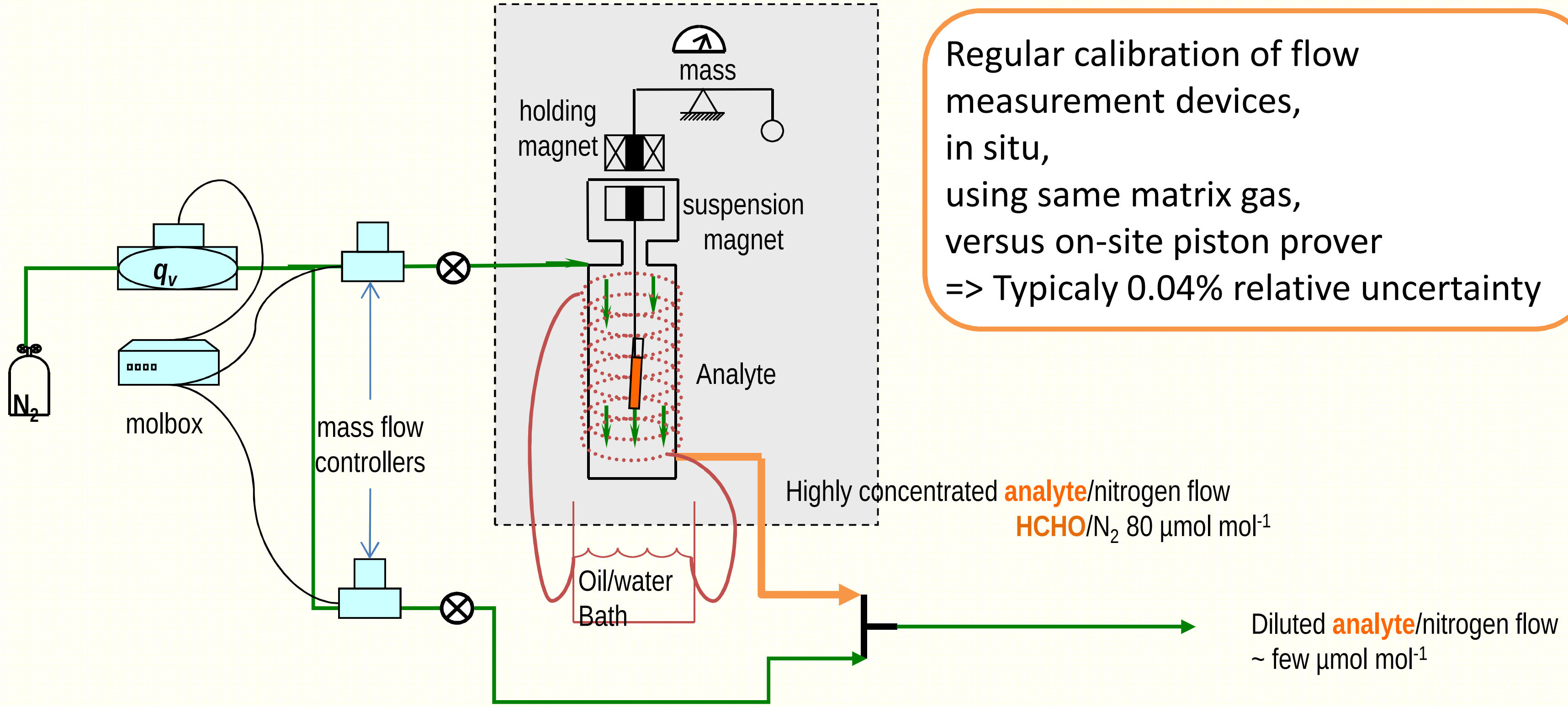


$$m(t) = m_0 + q_m t + \delta q_m t^2$$

- m_0 → Mass of the source
- q_m → Mass loss rate
- δq_m → Drift

Target : RSD < 10 µg in order to obtain typical relative uncertainty **< 0.1%**

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

Purity analysis

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

Analyte amount fraction **if pure**

$$x_A = \frac{q_m V_m}{q_v M} - \sum_i \frac{M_i x_i}{M_A} - \sum_j x_j$$

Impurities from **reaction with analyte**

Impurities **in the source**

Contribution of impurities can be large!

Analyte	Amount fraction / nmol mol^{-1}	Main impurity	Amount fraction / nmol mol^{-1}	Uncertainty contribution
NO_2	8860	HNO_3	104	88.9%
HCHO	2030	H_2O	12	79.5%
HNO_3	456	H_2O	750	81.15%

Purity analysis by FTIR

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

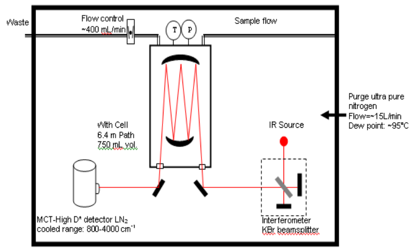
Database of spectroscopic parameters
(**HITRAN** or PNNL or NIST library)

```
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
. . .
```

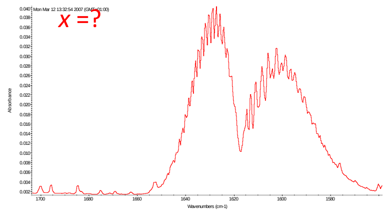
Synthetic calibration – uncertainty driven by database
5-10 %

Gas standard calibration –
uncertainty driven by gravimetry
< 1%

FTIR

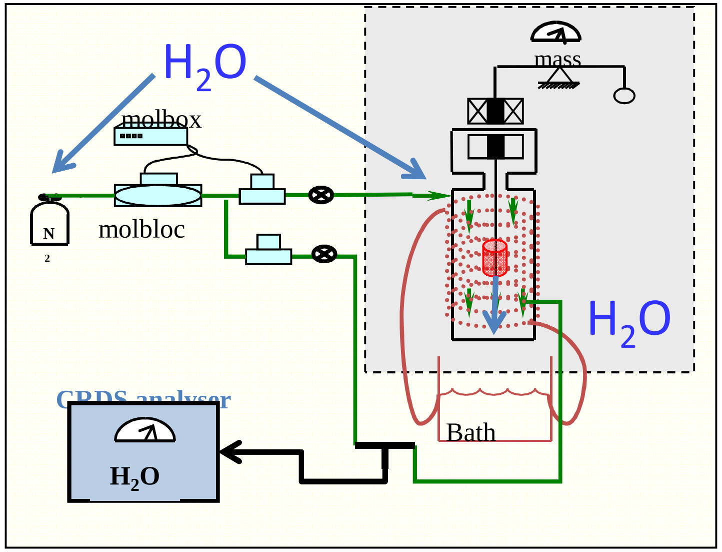


Measured spectrum



Water as impurity

FTIR : not appropriate to analyse trace water (large cell, leaks, …)
CRDS : specific analyser, good a trace levels

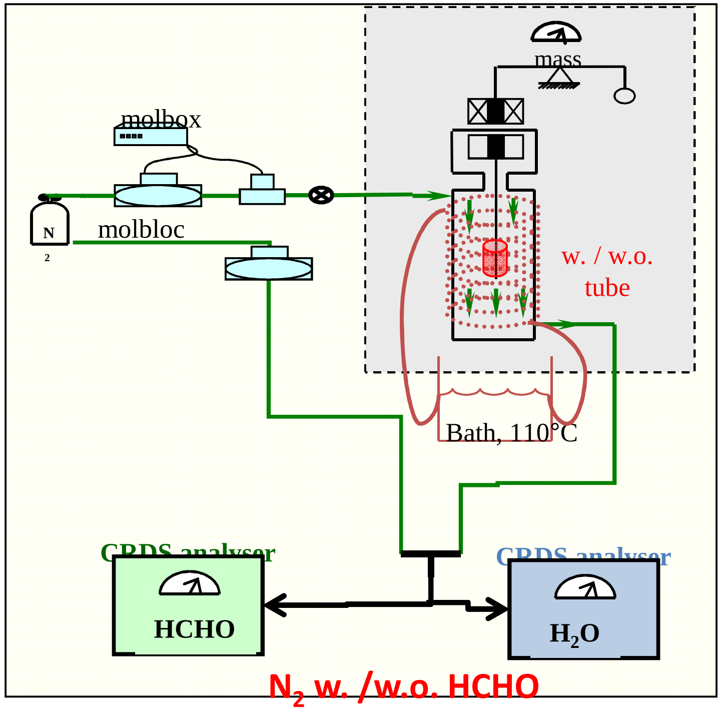


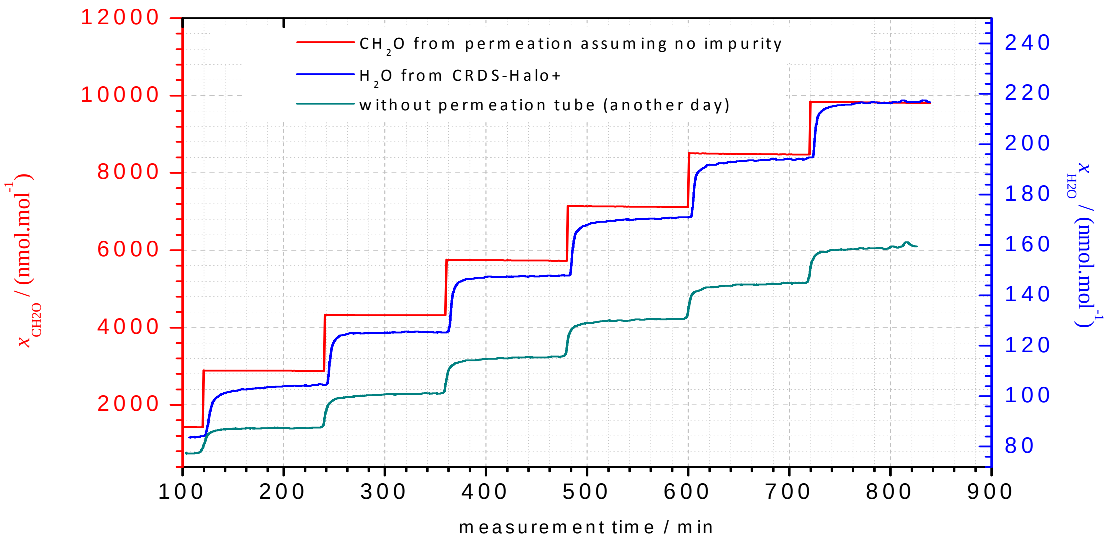
Specific precautions:

- Stainless steel chamber
- Coated tubes
- Dry nitrogen as matrix
- Calibration of water CRDS analyser ~ 5% uncertainty

Water quantification in HCHO from paraformaldehyde

Distinction to be made between water from the source / water from the system

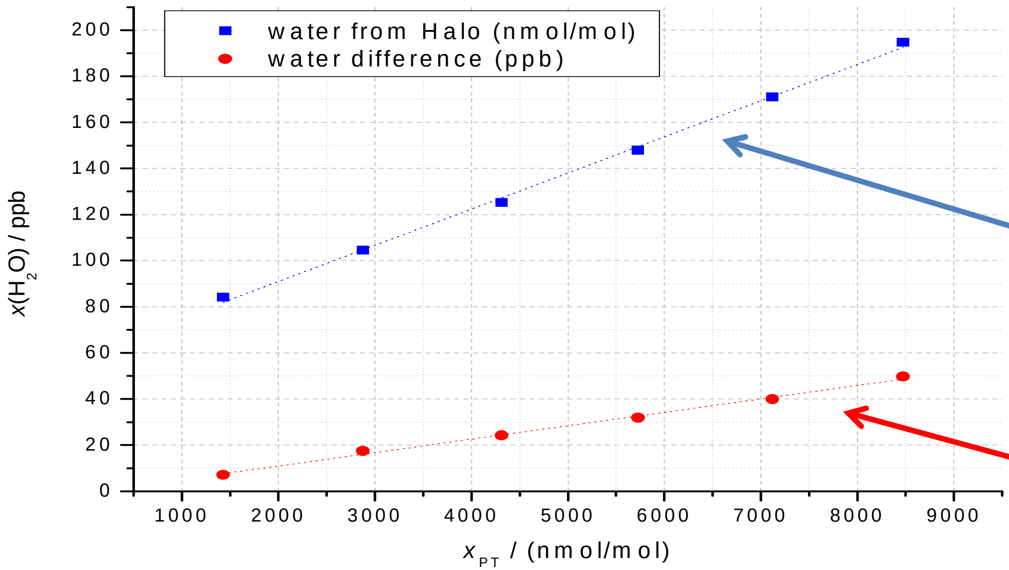




Evidence of lower H_2O without tube

Water quantification in HCHO from paraformaldehyde

Linear regression of the data from the graph:

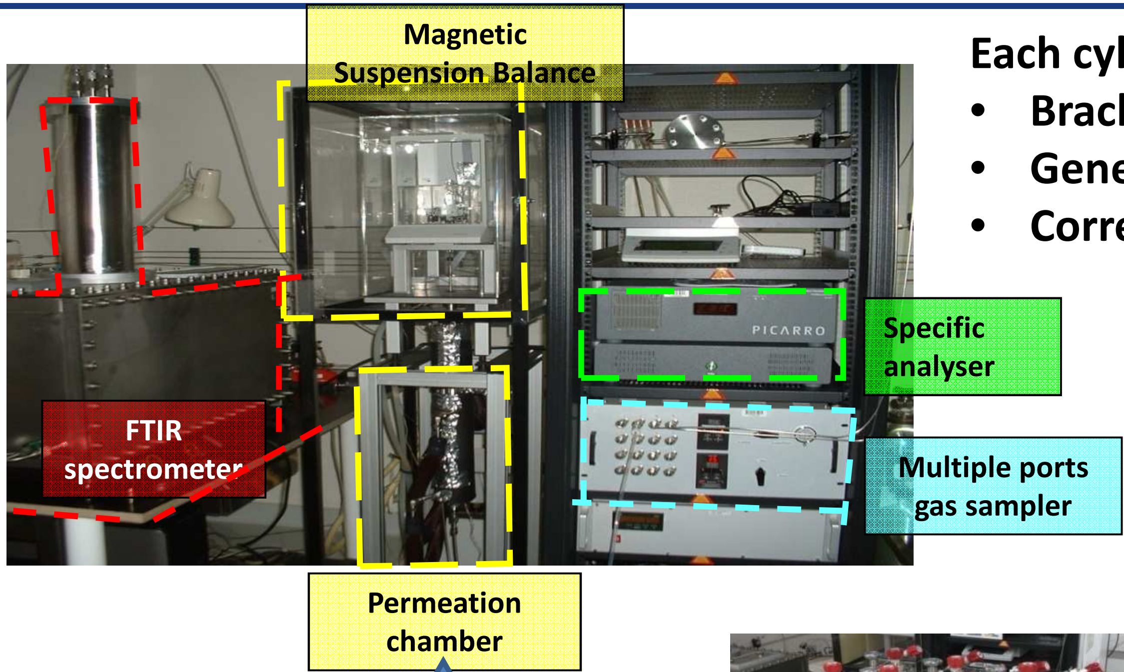


Total water mole fraction measured equivalent to 1.5% of mass loss

0.6% of mass loss is water permeating from Paraformaldehyde tube

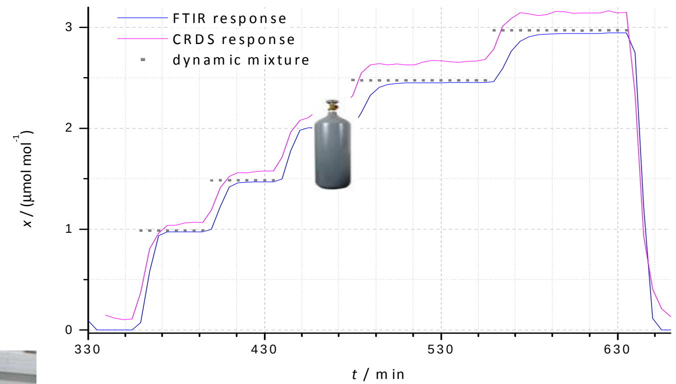
	Intercept Value	Intercept Standard Error	Slope Value	Slope Standard Error	Statistics Adj. R-Square
water from Halo	59.60407	1.89608	0.01568	3.42202E-4	0.99762
water difference	-0.68917	1.01861	0.00582	1.83837E-4	0.99504

Value assignment of mixtures in cylinder



Each cylinder is value assigned

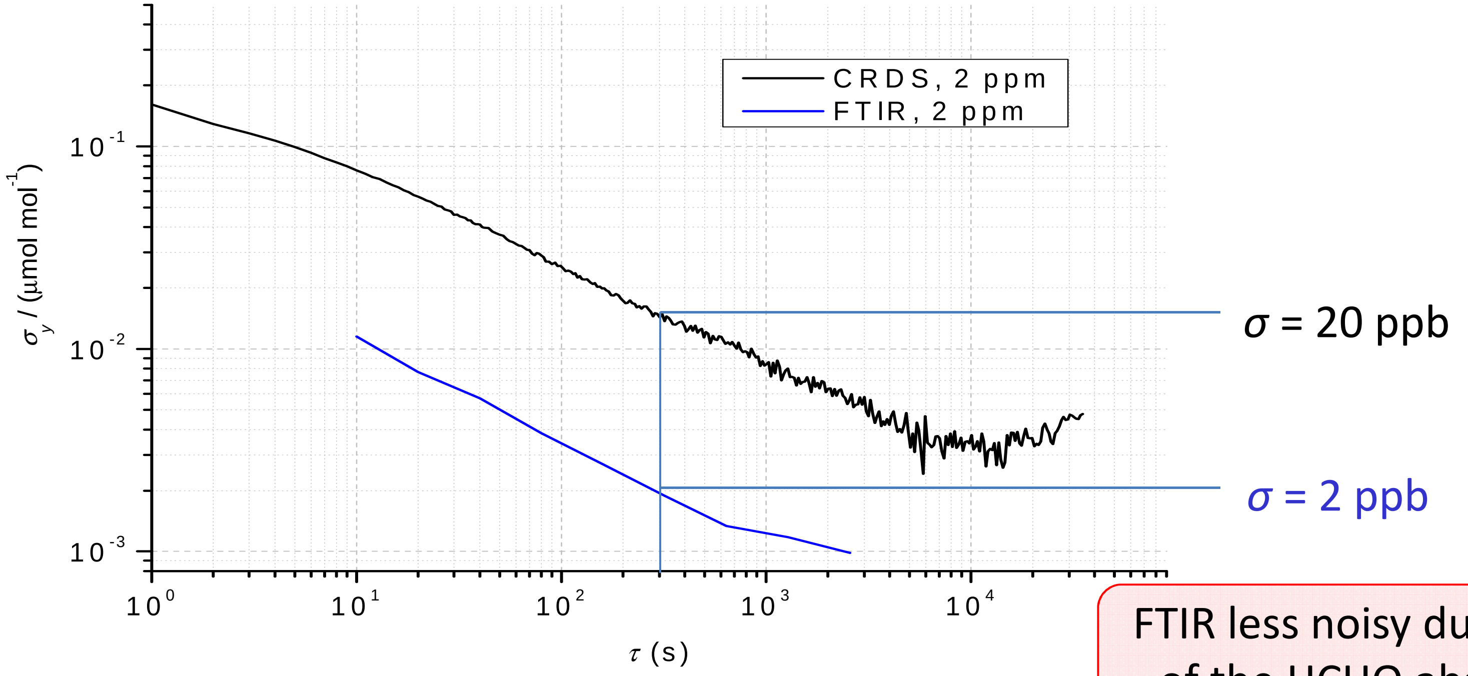
- **Bracketing with 4 dynamic values**
- **Generalised Least-Square fit**
- **Correlation between dynamic mixtures**



One cylinder value assignement sequence (~ 300 min)

Stability of analytical instruments

FTIR and CRDS stability compared on 2 µmol mol^{-1} of formaldehyde/nitrogen



FTIR less noisy due to the choice of the HCHO absorption band

Uncertainty of dynamic calibration gas

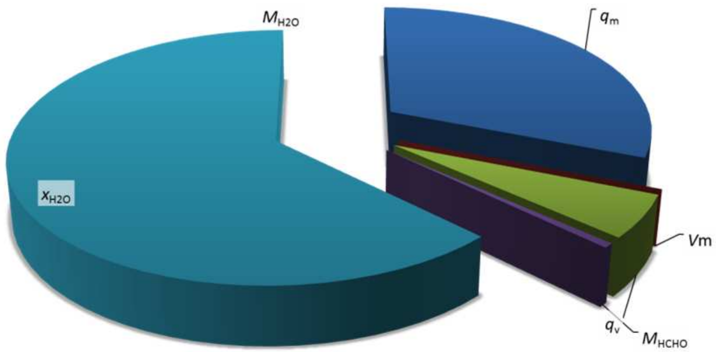
HCHO from paraformaldehyde

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}

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

Uncertainty calculations performed with Labview code

- $q_m(t)$ 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



Uncertainty of dynamic calibration gas

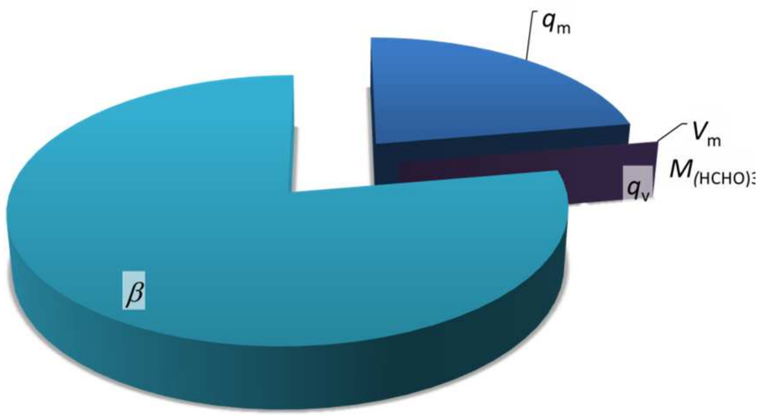
HCHO from trioxane

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}
$M_{(HCHO)3}$	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}

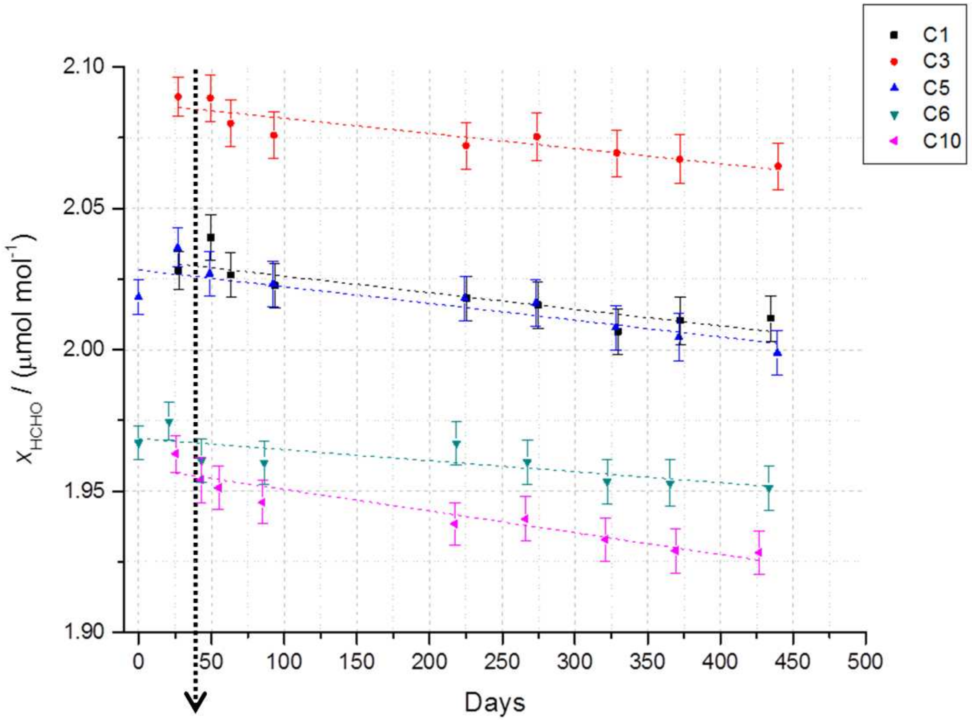
Uncertainty calculations performed with Labview code

- $q_m(t)$ 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



Gas Standard Value Assignment and Stability Monitoring

HCHO mole fraction decrease



No impact of switching permeation source

Series of measurements

- With paraformaldehyde source first month
- With trioxane source after 30 days
- FTIR as main analytical instrument
- Model linear trend

x_0 fitted value at time 0

a_1 HCHO loss in µmol mol^{-1} day^{-1}

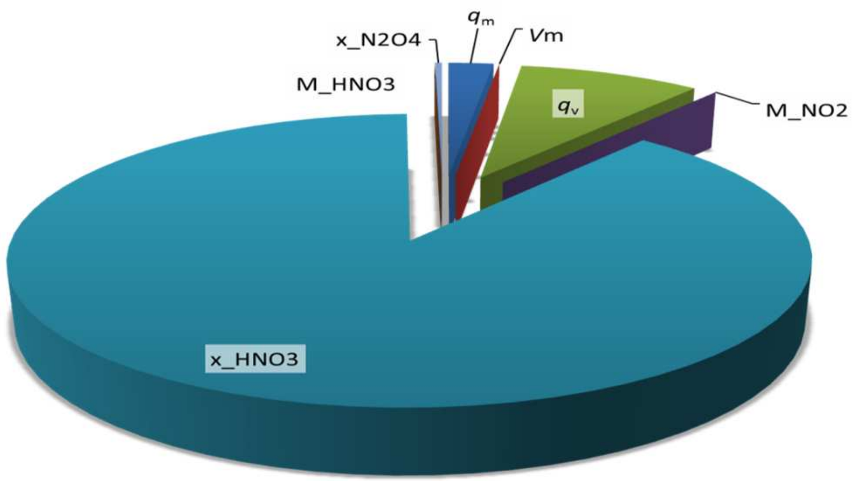
t measurement time in days

$$x(t) = x_0 + a_1 t$$

NO_2 standard value assignement with dynamic methods

Quantity	Value	unit	Standard relative uncertainty
q_m	8357.30	ng min^{-1}	5.00×10^{-4}
Vm	22.40037	L mol^{-1}	1.52×10^{-5}
q_v	0.452	L min^{-1}	1.00×10^{-3}
M_{NO2}	46.0055	g mol^{-1}	3.04×10^{-5}
x_{HNO3}	104.00	nmol mol^{-1}	2.02×10^{-1}
M_{HNO3}	63.013	g mol^{-1}	1.86×10^{-5}
x_{N2O4}	0	µmol mol^{-1}	0.866 nmol/mol

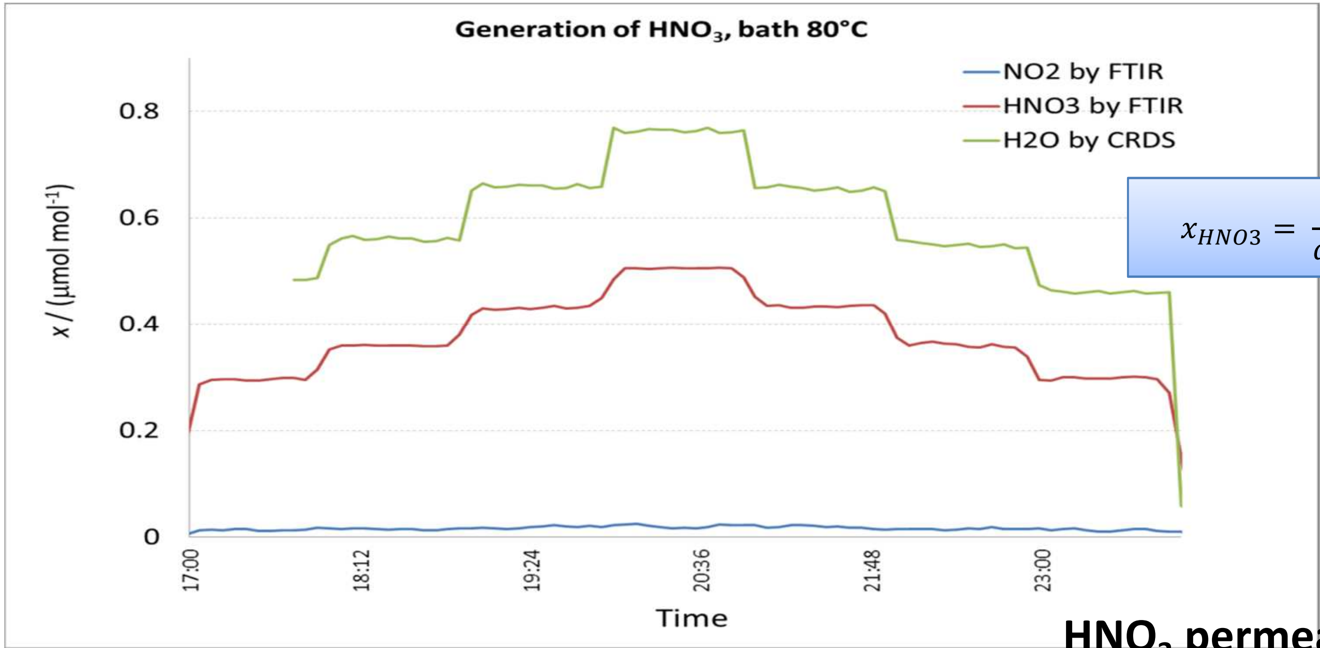
Quantity	Value	Standard Uncertainty
$x(NO_2)$	8.86 µmol mol^{-1}	0.03 µmol mol^{-1}



HNO_3 quantification by FTIR referenced to molecular parameters (HITRAN)

Reducing the uncertainty of HNO_3 measurements

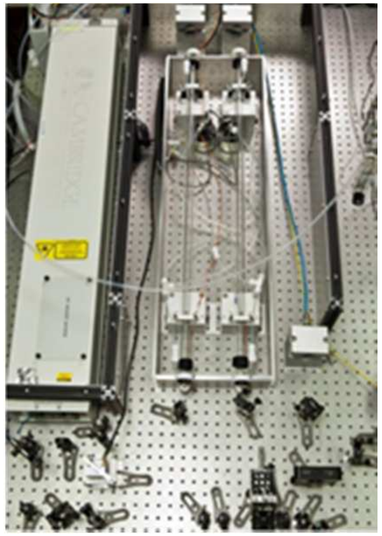
Generation of dynamic mixtures of HNO_3 in nitrogen by permeation



$$x_{HNO3} = \frac{q_m\,Vm}{q_v\,M_{HNO3}} - \frac{M_{NO2}x_{NO2}}{M_{HNO3}} - \frac{M_{H2O}x_{H2O}}{M_{HNO3}}$$

HNO_3 permeation [200-500] nmol mol^{-1}
Permeation rate ~ 30 % H_2O
H_2O accurate quantification is crucial

Spectroscopic Methods



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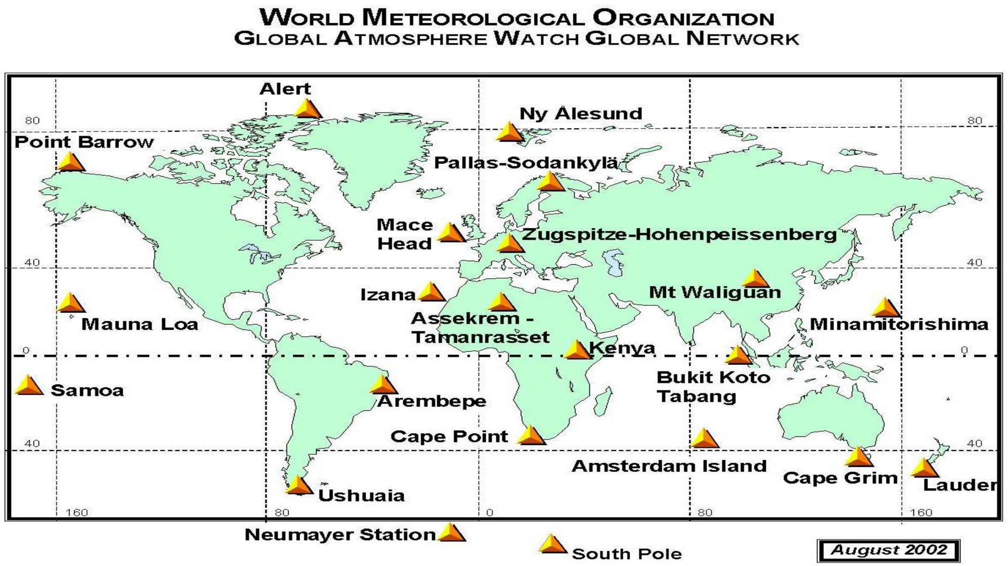
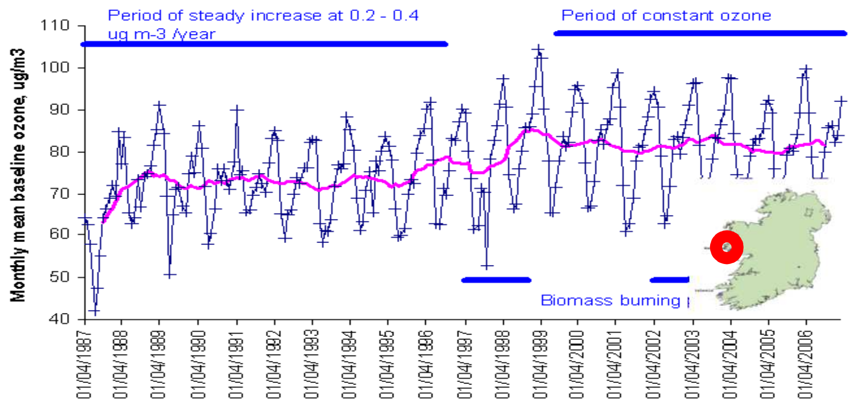
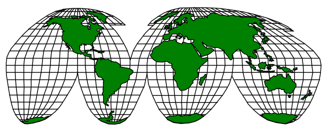
Surface Ozone Standards



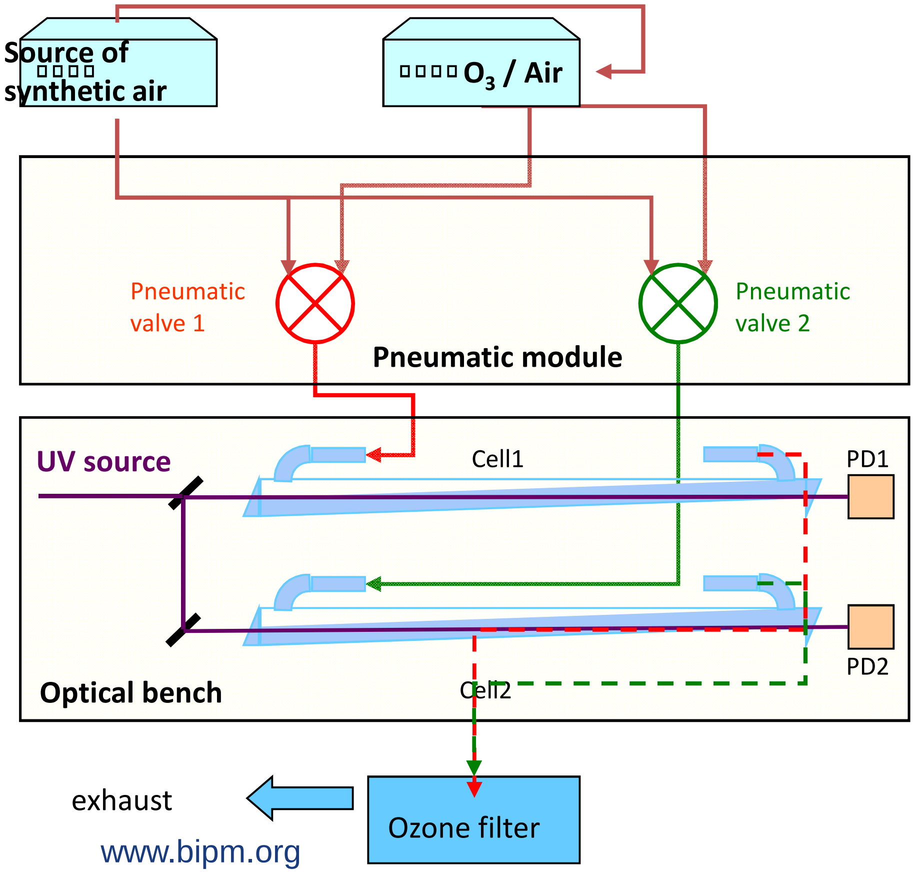


BIPM-NIST program to maintain the comparability of the worldwide network of ozone reference standards



NIST BIPM

Principle of an ozone photometer



www.bipm.org

- **Ozone generator** to produce ozone by photolysis of oxygen in the range 10 nmol mol^{-1} to 1000 nmol mol^{-1}
- **Pneumatic module** to alternatively direct ozone/air gas flows in the two gas cells
- **Optical bench** with light source, optics, gas cells and detectors to perform absorption measurements

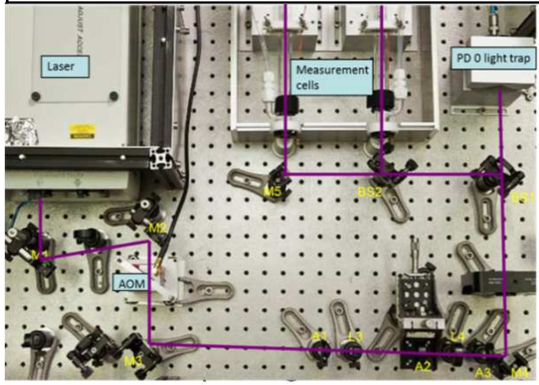
Measurement Equation:

$$x = \frac{-1}{2\alpha L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln(D)$$

x /(nmol mol^{-1})	: ozone mole fraction in air
P / Pa	: Cell pressure
T / K	: Cell temperature
L_{opt} / m	: Light path length
D	: product of transmittances in both cells
α / cm^{-1}	: linear absorption coefficient

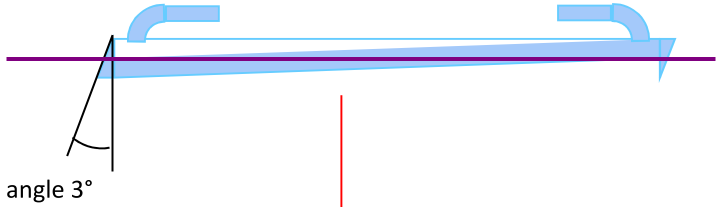
Laser ozone photometer optical setup: Uncertainty budget

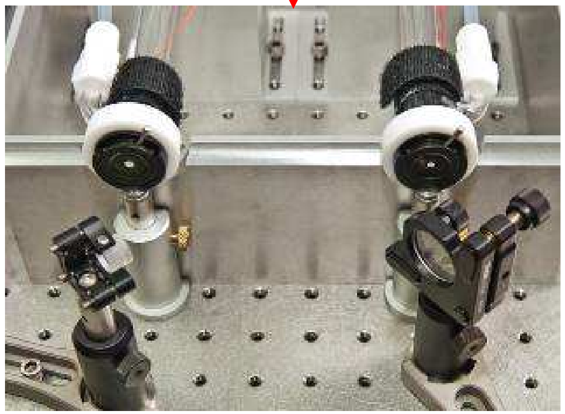
Parameter	value	Standard uncertainty	Relative uncertainty
Temperature T	295 K	0.061 K	2.1×10^{-4}
Pressure P	1000 mbar	0.64 mbar	6.4×10^{-4}
Optical length L_{opt}	893.9 mm	0.4 mm	4.5×10^{-4}
Product of transmittances D	0.95	1.2×10^{-5}	2.6×10^{-4}
Combined relative uncertainty (without the absorption cross-section)			8.5×10^{-4}



Major improvement compared to SRP = reduced uncertainty on the path length.

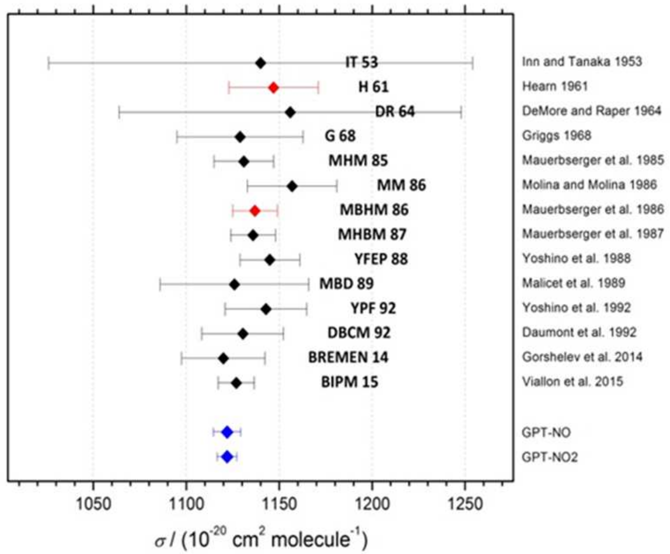
Cells windows not perpendicular to laser beam



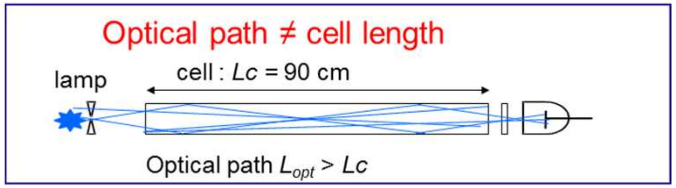


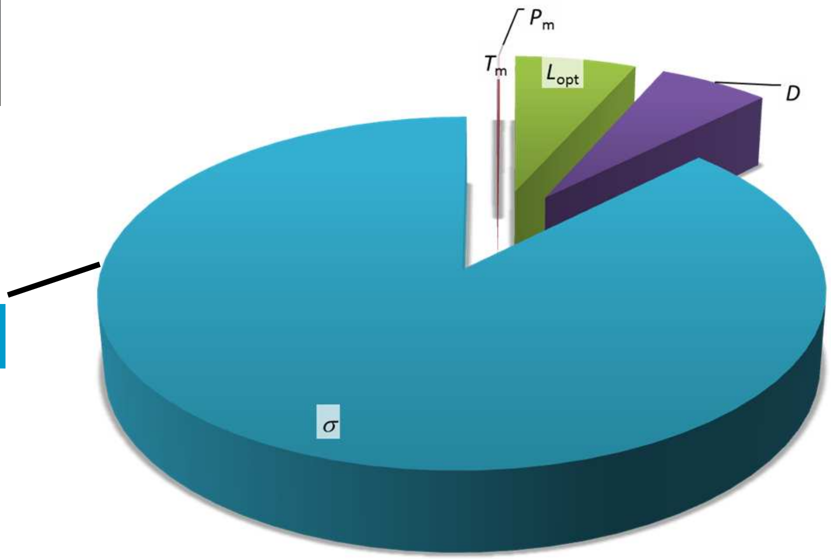
3 mm diaphragm before/after cells to help laser alignment

Uncertainty budget



Light path cell inside the gas cell





Absorption cross-section

Fundamental property of the molecule
Measured separately on known amount fractions
Measured by ~ 15 groups
Conventional value to be adopted

FTIR equipment and calibration strategies

FTIR hardware

Nexus spectrometer
Vertex 70v Vacuum FTIR (<1 hPa)
2- 0.7 L gas cells (Electropolished and Silcosteel)
1- 7 L gas cell (Silcosteel)

Software

MALT 4.4 (HITRAN)
MALT 5 (HITRAN)
P-MALT (MALT)
IMACC (Synthetic spectra or measured spectra)
E-TRANS (HITRAN)

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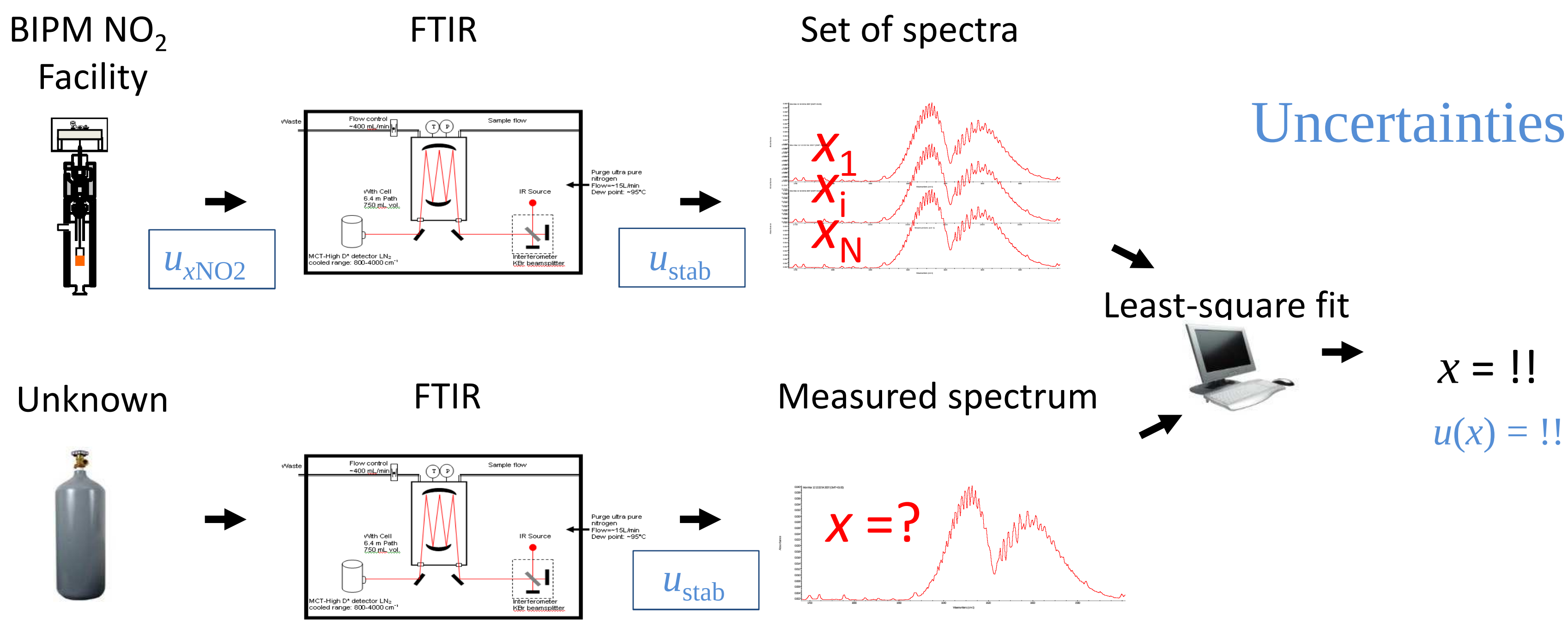
Using FTIR with and without calibration standards



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Using FTIR with and without calibration standards

HITRAN

Database of line strengths
+
Spectrometer characteristics
(L_{opt}, aperture, resolut

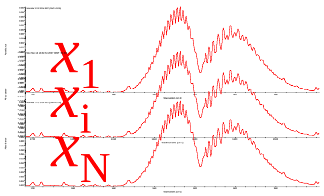
u_{HITRAN}
$u_{P1}, u_{Pi}, \ldots$

MALT

Software simulating the spectrometer response

$u_{MALT\text{-}CLS}$

Set of spectra



x_1
x_i
x_N

Uncertainties

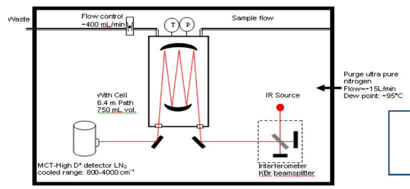
Least-square fit

x = !!

$u(x)$ = !!

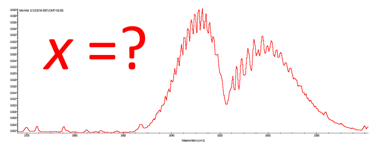
Unknown

FTIR



u_{stab}

Measured spectrum



x =?

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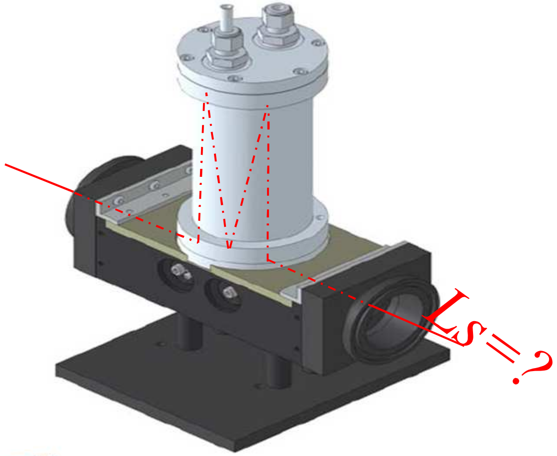
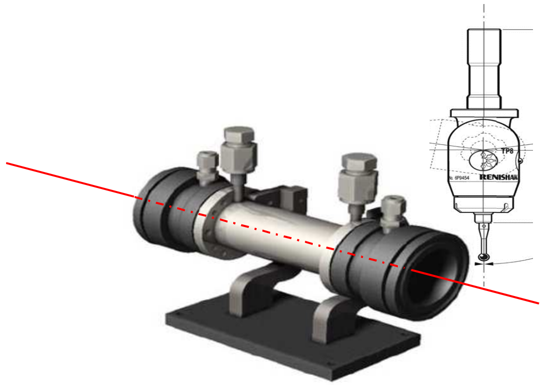
Pathlength uncertainty L_{opt}

Determination of the White-cell's path length

Use	Origin	#Cylinder	Assigned NO_2 mole faction $\mu mol \cdot mol^{-1}$	Certified standard uncertainty $\mu mol \cdot mol^{-1}$ (%)		Matrix gas
Reference	NPL	L1000025	99.99	0.8	(0.8)	Nitrogen/Oxygen
Sample	VSL	680178	11.00	0.22	(1.0)	Nitrogen



$$\left(\frac{C_s L_s P_s}{Ts}\right) = K * \left(\frac{C_r L_r P_r}{T_r}\right)$$



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100 Ω RTD temperature probe placed into the gas cells, with standard uncertainty u_{T1} = 0.02 K

Barometer (Series 6000) uncertainty u_p =0.04 %.

Uncertainty of applying spectral fitting … (MALT)

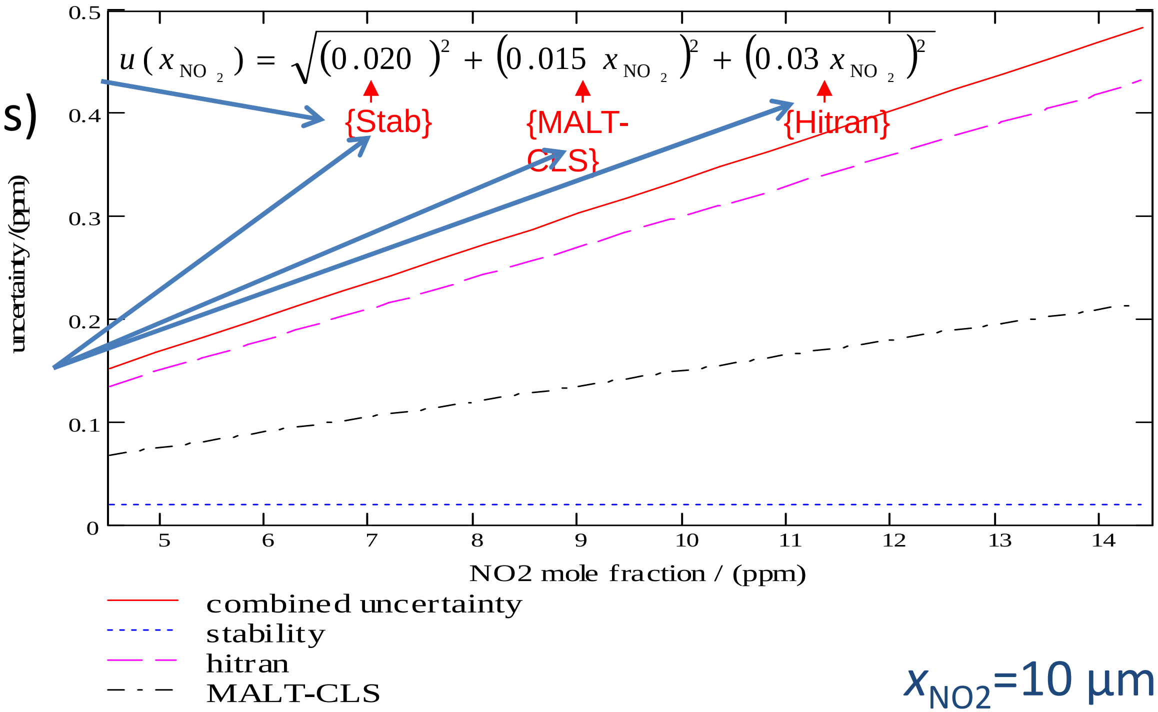
MALT input parameter	Estimated value x_i	Unit	Assumed distribution	Standard uncertainty $u(x_i)$	Measurand variation DY	Index to uncertainty DY/2	Index to uncertainty in %
Pathlength	6.45	m	normal	0.085	-0.258	-0.13	61.04
Temp	27.7	℃	normal	1.37	0.175	0.09	28.08
Amount	10	µmol/mol	rectangular	1	-0.075	-0.04	5.16
% halfwidths for Voigt	50	cm^{-1}	rectangular	20	-0.059	-0.03	3.19
Resolution	0.964	cm^{-1}	rectangular	0.062	0.052	0.03	2.48
Colimator appertures	4.666	mm	rectangular	0.1	-0.005	0	0.02
Presure	794	Torr	normal	0.159	0.004	0	0.01
Region <1600 cm-1	1660	cm^{-1}		0		0	0
Region >1600cm-1	1550	cm^{-1}		0		0	0
% halfwidths	5	%	rectangular	3	0	0	0
Colimator focal length	152	mm	rectangular	1	0	0	0
SYm1	0	-	rectangular	0.1	0.001	0	0
SYm2	0	-	rectangular	0.1	0.0023	0	0
Wavenumber shift rel to Hitran	0	cm^{-1}	rectangular	0.1	0	0	0
Base line offset	0	cm^{-1}	rectangular	0.3	0	0	0

NO_2 mole fraction x = 11.08 µmol/mol combined uncertainty u(x) = 0.165 µmol/mol $u_R(x)$ = 1.50%

Total uncertainty:

Mode A
(With standards)

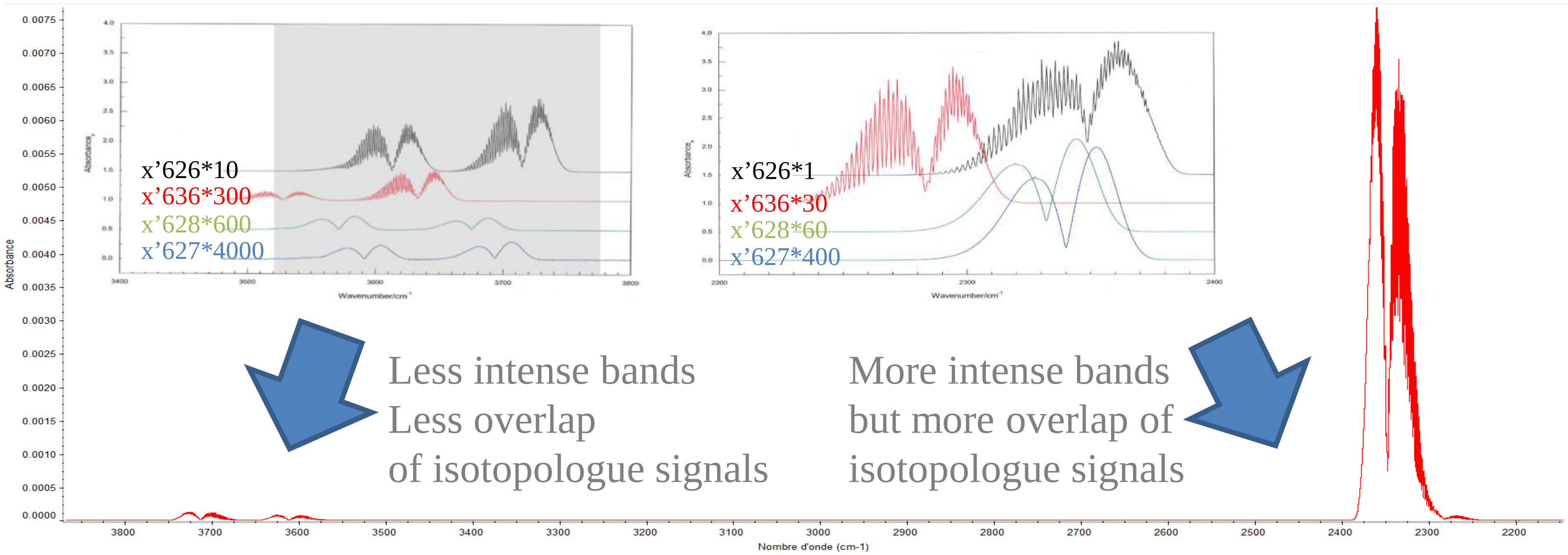
Mode B
(Without
standards)



Numerical equation in µmol mol^{-1}

x_{NO2}=10 µmol mol^{-1}

Measurement of CO_2 (and CO_2 isotopologues) by FTIR



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Accurate measurement of CO_2 (and CO_2 isotopologues) by FTIR

M/z	CO_2 Isotope
44	$^{12}C^{16}O_2$
45	$^{13}C^{16}O_2$, $^{12}C^{16}O^{17}O$
46	$^{12}C^{16}O^{18}O$, $^{13}C^{16}O^{17}O$, $^{12}C^{17}O_2$
47	$^{13}C^{16}O^{18}O$, $^{12}C^{17}O^{18}O$, $^{13}C^{17}O_2$
48	$^{13}C^{17}O^{18}O$, $^{12}C^{18}O_2$
49	$^{13}C^{18}O_2$

Isotope ratio: $\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}$

$$\delta^{13}\mathrm{C} = \frac{\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}(sample) - \frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}(standard)}{\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}(standard)}$$

Traceability Chain for δ-scale CO_2 isotope ratio measurements

CO_2 (pure): $\delta^{13}C$, $\delta^{18}O$

Measurand and Unit- Definition

IAEA

NBS 19, LSVEC
(Fix VPBD scale and second calibration point)

Phosphoric acid reaction and mass spec measurement procedure
(Peer reviewed literature)

NIST

Reference Materials across scale
RM8562, 8563, 8564

Mass spec measurement procedure
(Peer reviewed literature)

University Laboratory

Working Standards in specialist laboratory (University)

Mass spec measurement procedure
(Peer reviewed literarture)

Specialty Gas Industry

Commercially Available Standards

End user Measurement Procedure

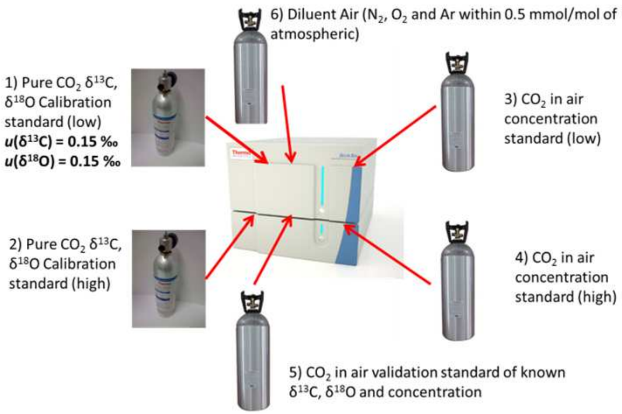
End User

RESULT
CO_2 in µmol/mol

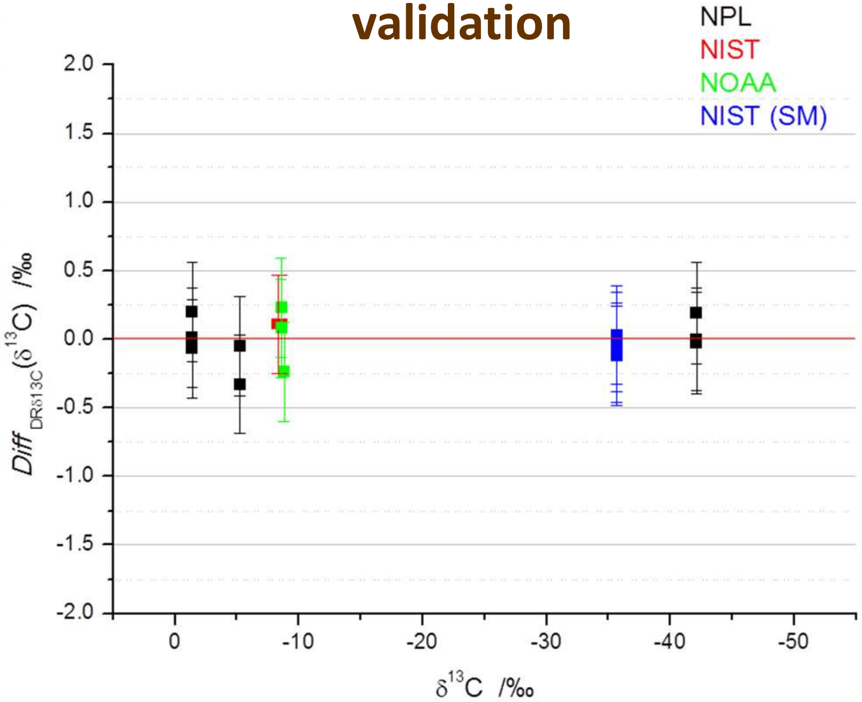
Measuring Carbon isotope ratios in CO_2 in Air

Quantity	Analytical Method	Range	Analytical Standard Uncertainty
X_{CO2}	FTIR	(300 to 850) µmol/mol	0.03 µmol/mol
X_{CO2}	IRIS	(300 to 850) µmol/mol	0.04 µmol/mol
X_{CO2}	GC	(300 to 850) µmol/mol	0.04 µmol/mol
X_{CO2}	PVT system	(300 to 850) µmol/mol	0.1 µmol/mol
$\delta^{13}C$ (CO_2)	IRIS	(-1 to -42)‰ (VPDB scale)	0.2 ‰
$\delta^{18}O$ (CO_2)	IRIS	(-1 to -34)‰ (VPDB scale)	0.4 ‰
$\delta^{13}C$ (CO_2)	FTIR	(-1 to -42)‰ (VPDB scale)	0.4 ‰
$\delta^{18}O$ (CO_2)	FTIR	(-1 to -34)‰ (VPDB scale)	3.0 ‰

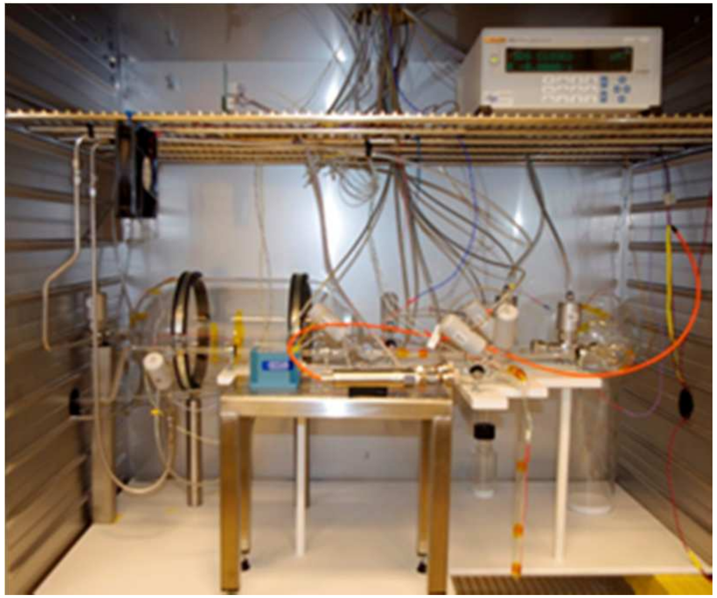
IRIS Calibration Sequence



$\delta^{13}C$ CO_2 measurement validation



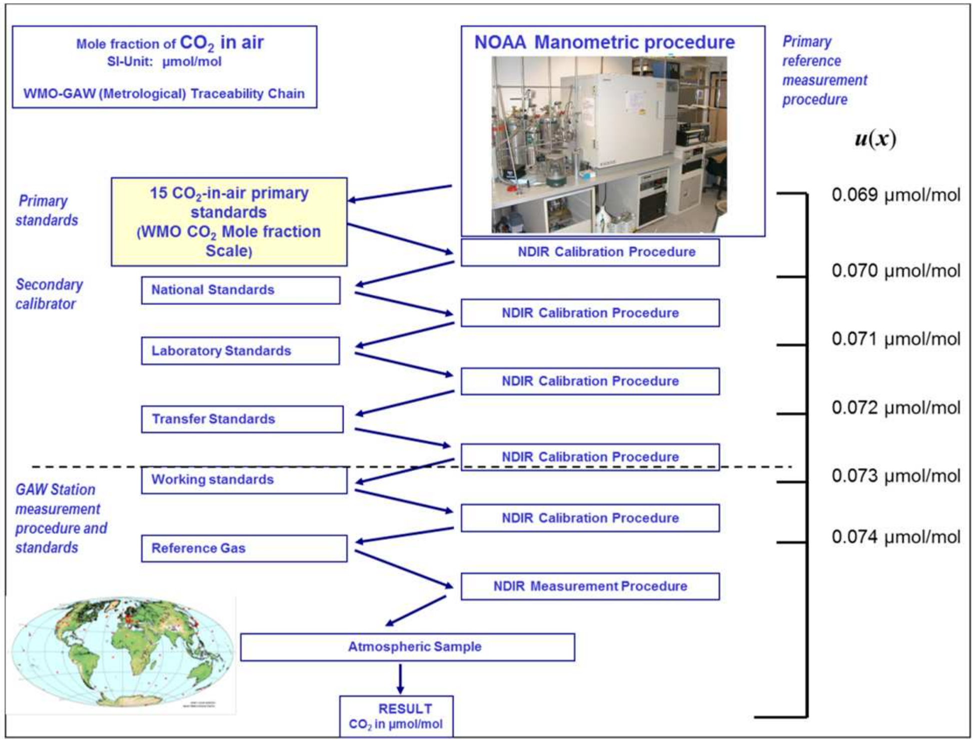
Manometric Methods

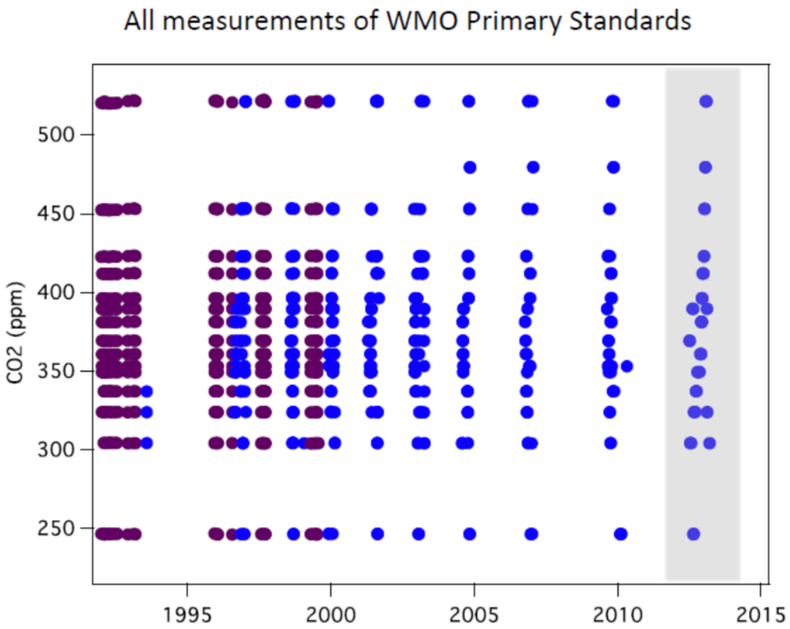


Carbon dioxide

WMO GAW network is the designated baseline network for CO_2 and CH_4

- NOAA/ESRL is the Central Calibration Laboratory for CO_2 and CH_4 (and other trace gases)





Manometry: Basic principle

- Initially well known amount of air, V_{air}, T_{air} and P_{air}.
- Extract CO_2 from the air by cooling
- Expand the CO_2 in another (smaller) well known volume, V_{CO2}, T_{CO2} and P_{CO2}

$$x_{CO2} = \frac{n_{CO2}}{n_{air}} = \frac{1}{R_V} \frac{P_{CO2}}{P_{air}} \frac{T_{air}}{T_{CO2}} \frac{1 + \frac{B_{air}(T_{air})P_{air}}{RT_{air}}}{1 + \frac{B_{CO2}(T_{CO2})P_{CO2}}{RT_{CO2}}}$$

$$R_V = \frac{V_{air}}{V_{CO2}}$$

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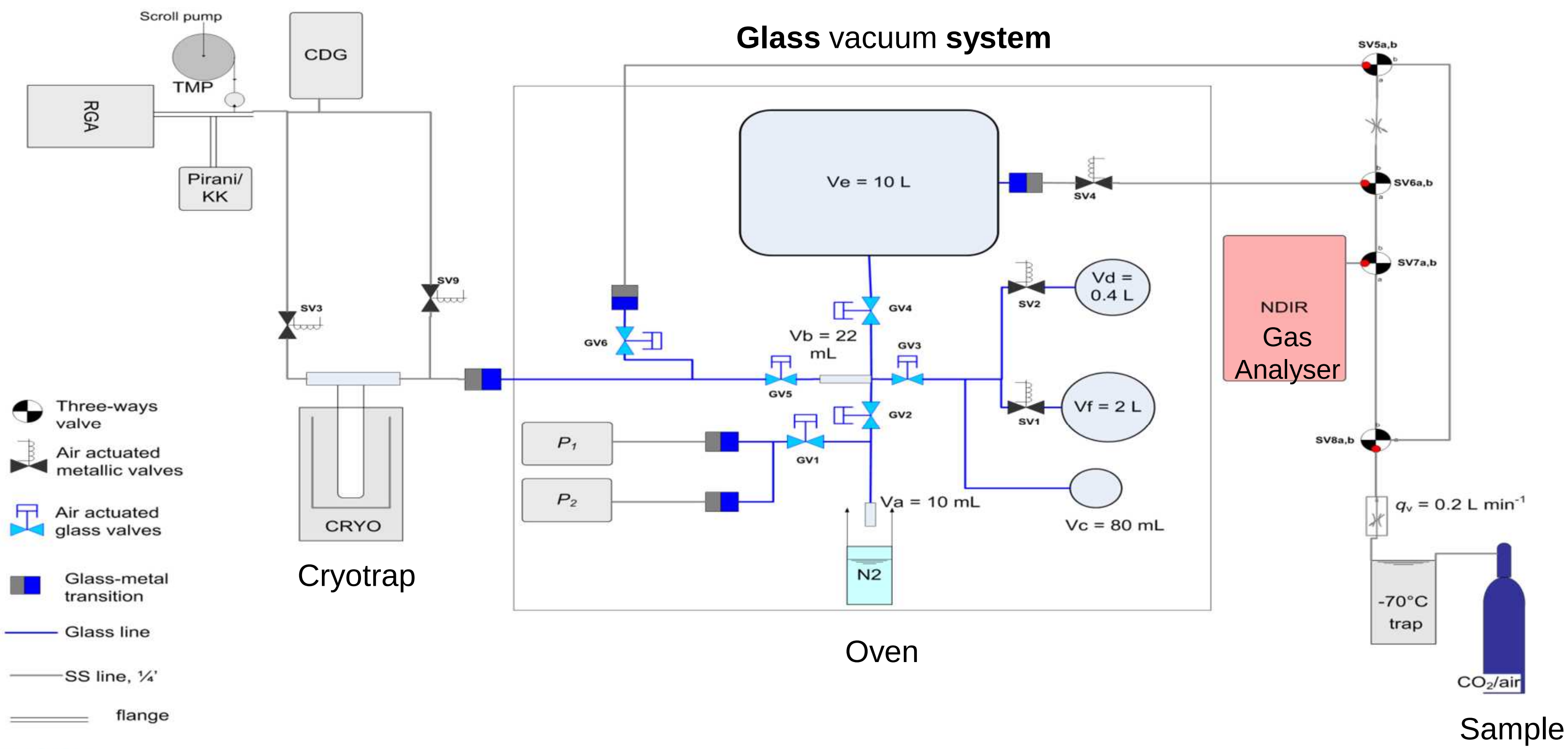
System layout: CO_2 Manometry



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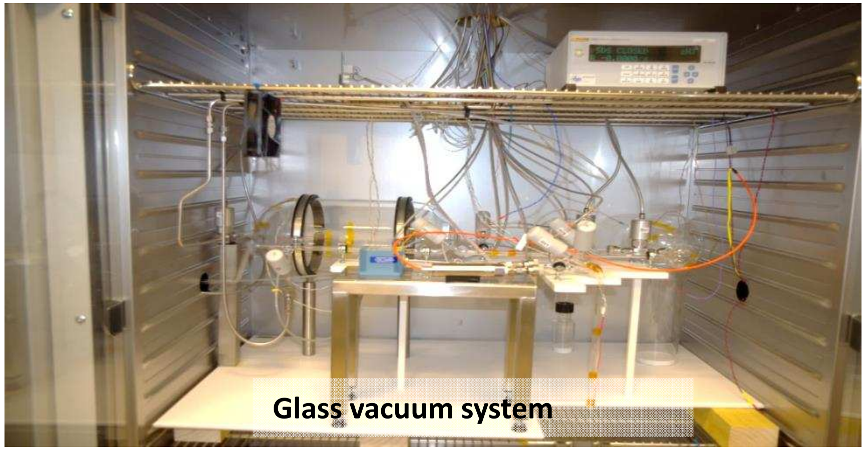
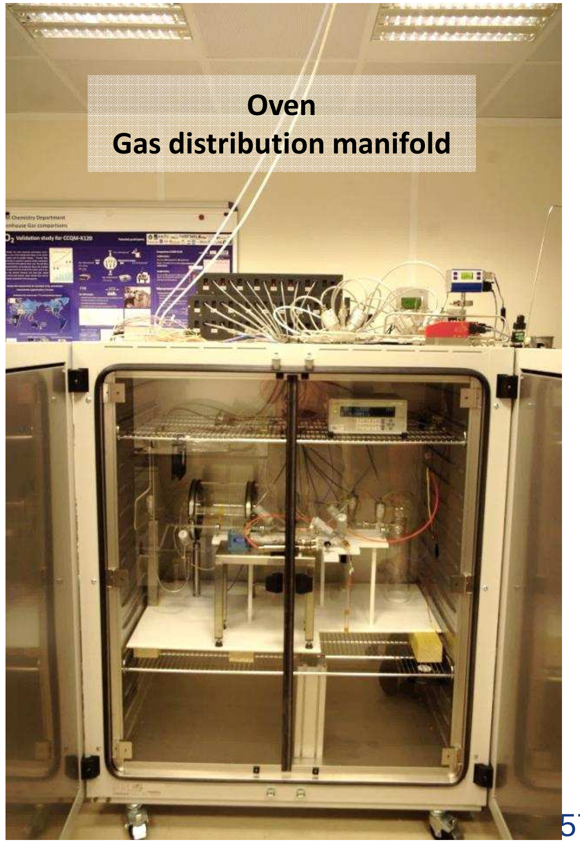
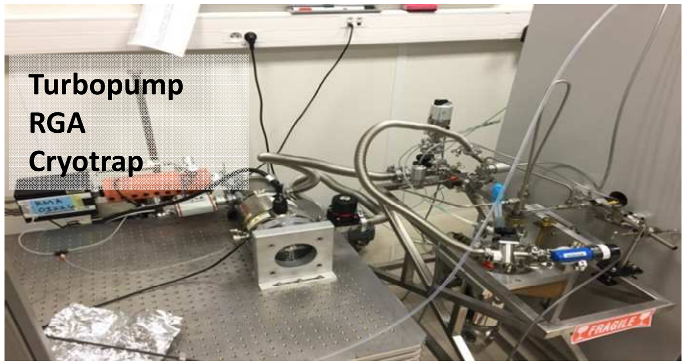
System overview







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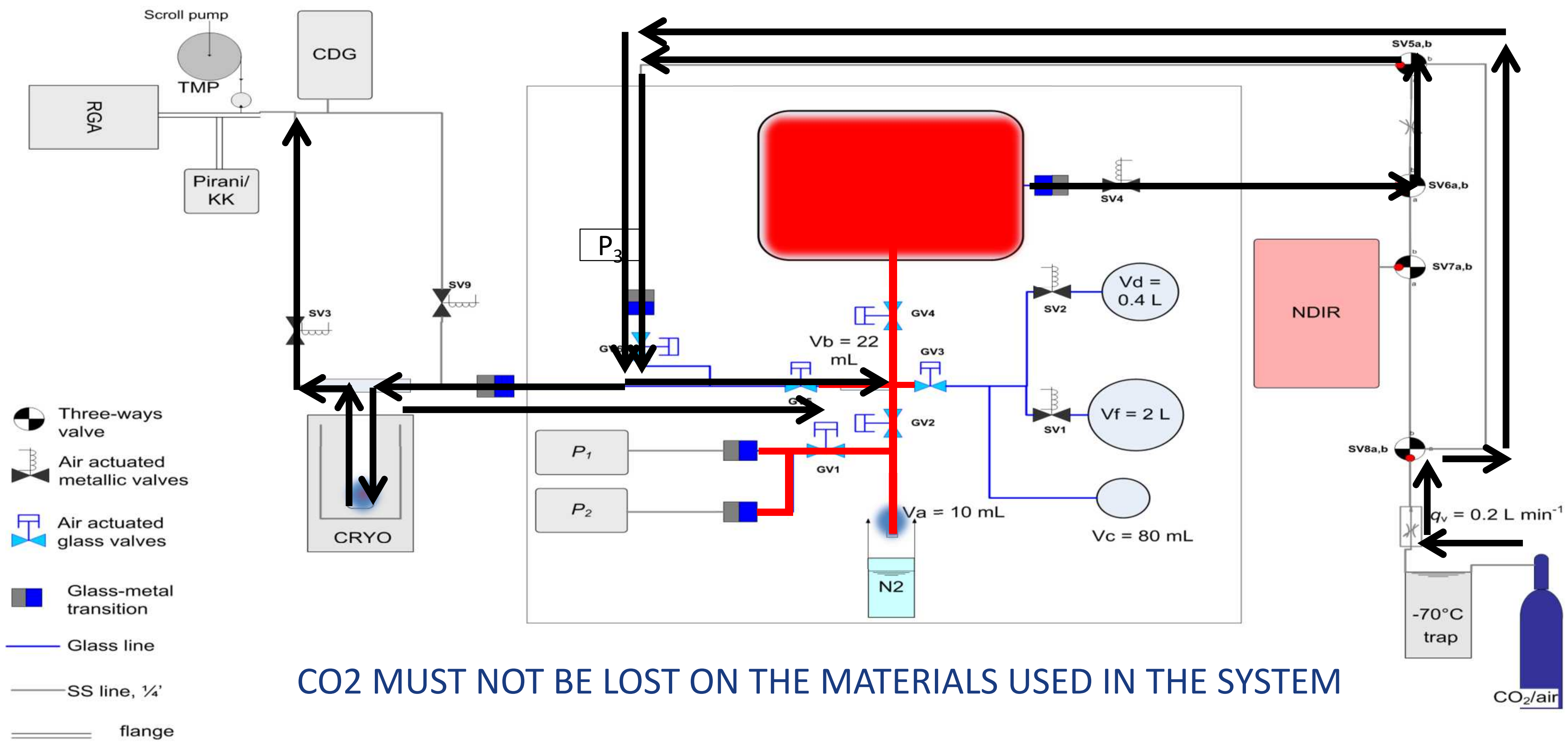
Principle of operation



CO2 MUST NOT BE LOST ON THE MATERIALS USED IN THE SYSTEM

Cold trapping

When **trapping**, should be:

- Hot enough to allow N_2, O_2, Ar, CH_4,N_2O to pass
- Cold enough to capture H_2O, and CO_2

When **distilling**, should be:

- Cold enough to keep H_2O,
- Hot enough to release CO_2

Needs to be:

- **Long enough** to make sure CO2 is fully captured (two mechanisms…possible issues)
- Made of materials that don't cause chemical reactions

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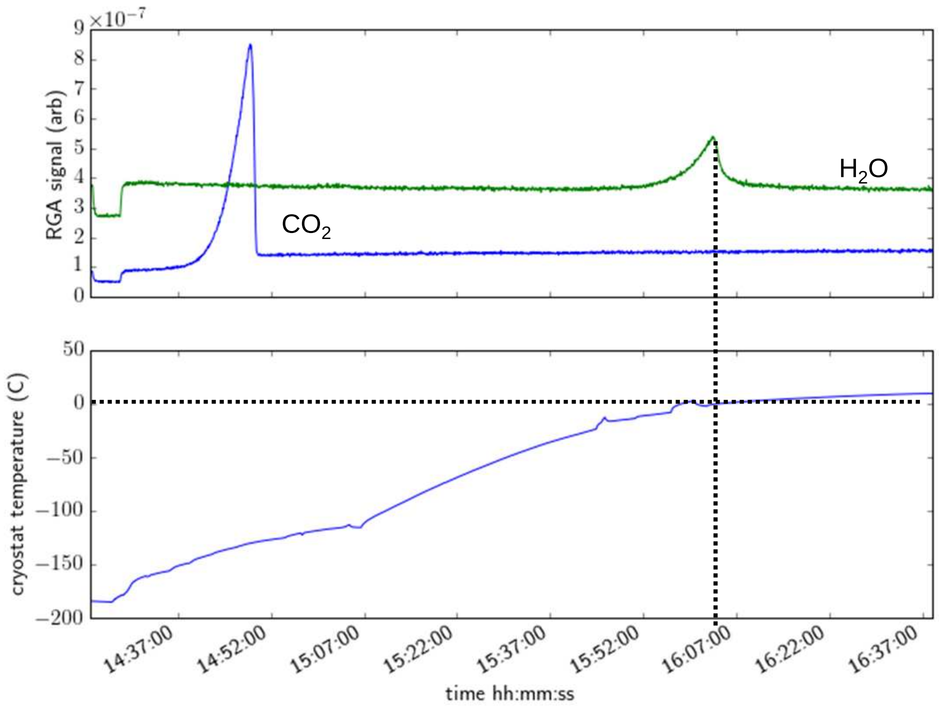
RGA can diagnose input cold trap



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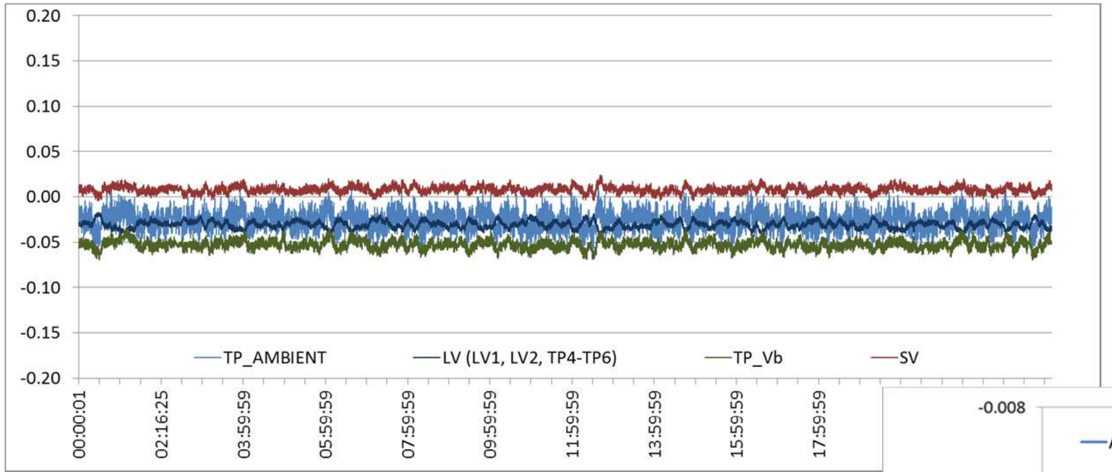
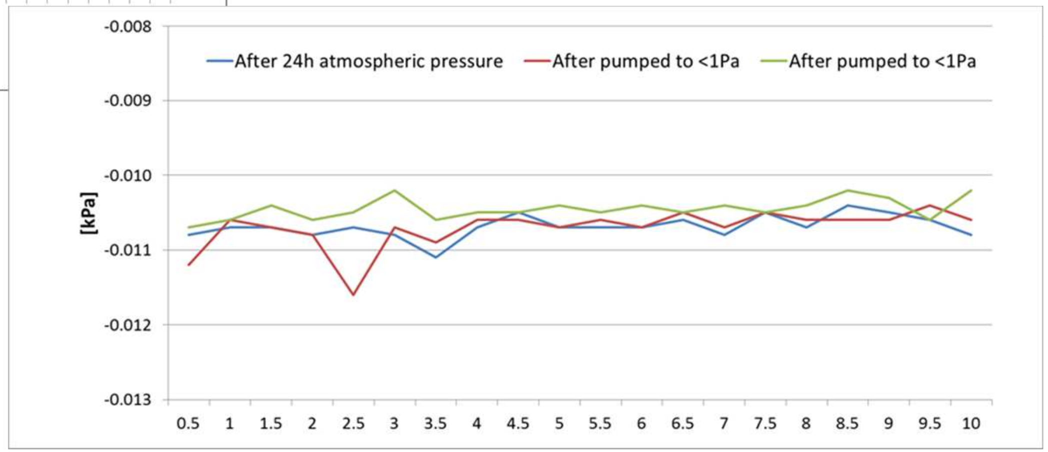
Temperature and Pressure Measurement

- **Temperature**: Differences below 0.05°C



Pressure Measurement at two distinct levels, 100 kPa and 30 kPa.



Comparison against external reference standard kept at 100 kPa.

Short term stability and hysteresis are excellent, well below 1 Pa.

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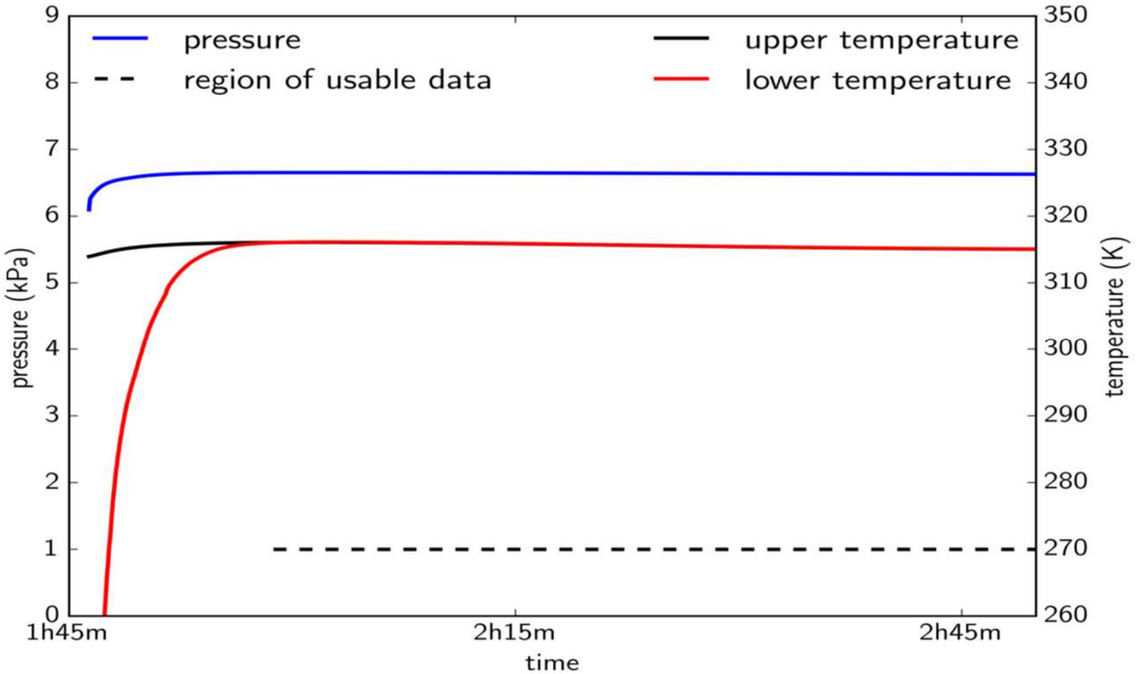
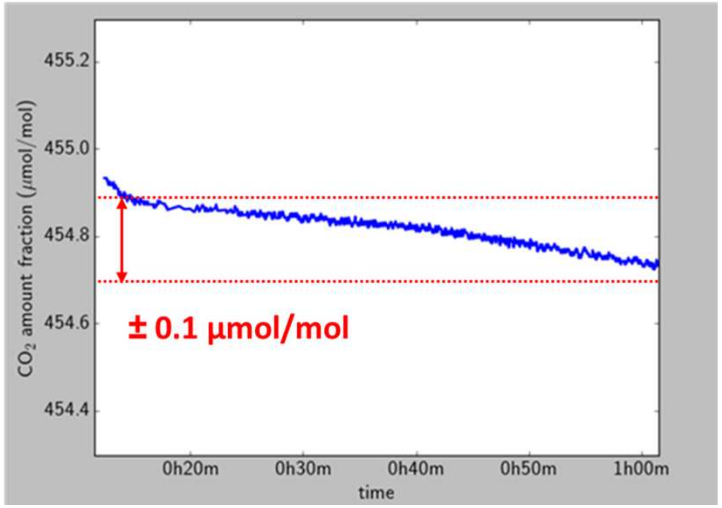
CO_2 Extraction sequence





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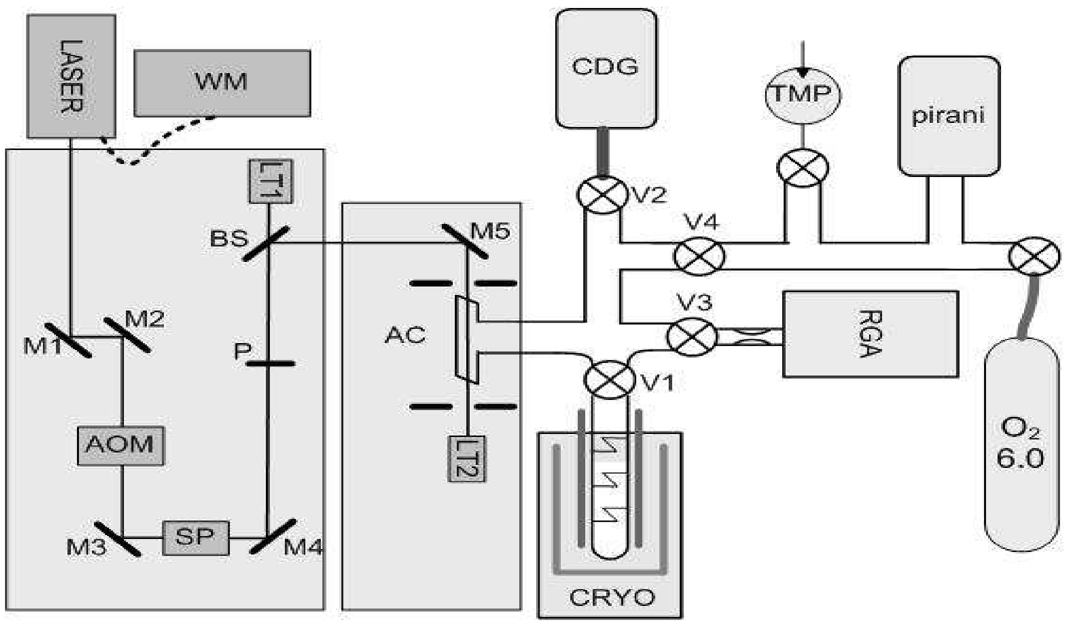
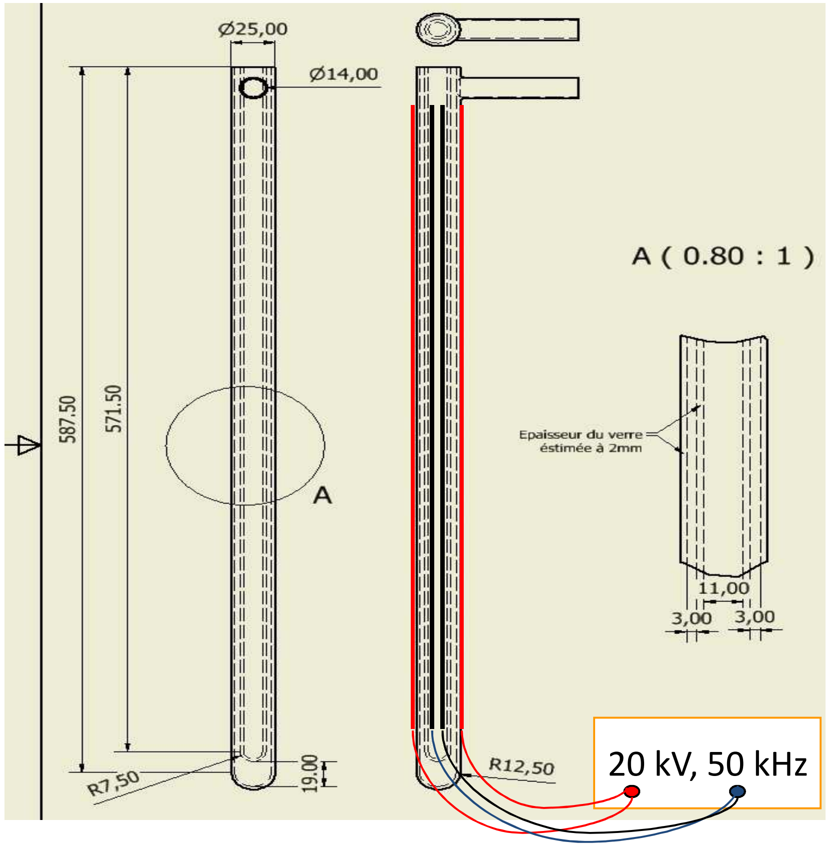
Manometric System for O_3 Cross Section Measurements

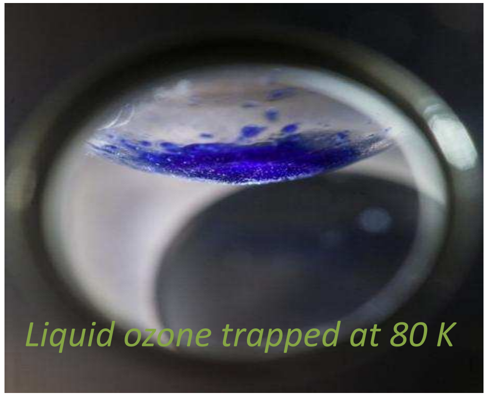


AOM Accousto-Optic Modulator;
BS Beam Splitter;
CDG Capacitive Diaphragm Gauge (Baratron);
CRYO Cryogenic ozone generator;
LT Light Trap;
M Mirror;
RGA Residual Gas Analyser ;
TMP Turbo Molecular Pump;
V Valve;
WM Wavemeter

Ozone generator

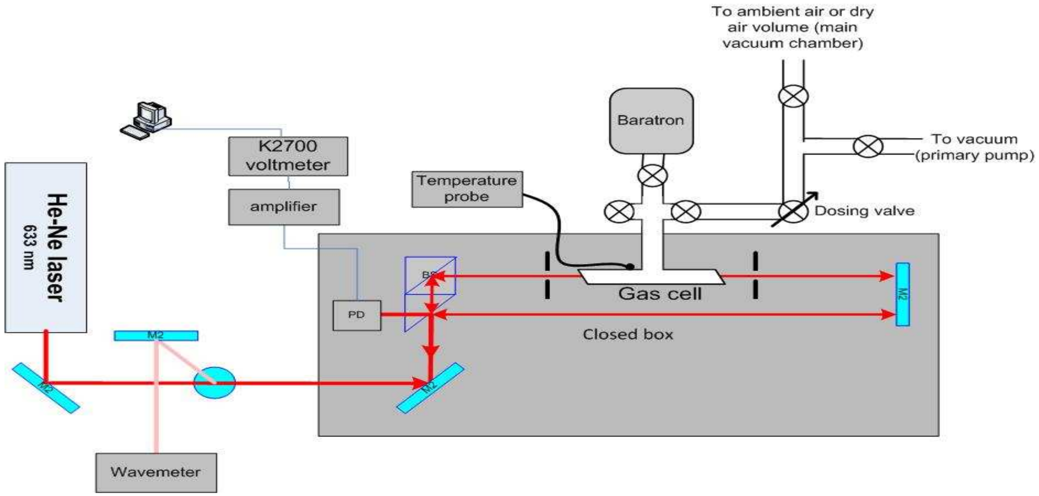


- **Ozone produced by discharges in pure oxygen**
- **generator = double wall cylinder in glass**
- **generation part inserted in cryostat**
- **controllable cryostat temperature from 74 K and above**


Liquid ozone trapped at 80 K

Absorption path length measurements by interferometry

Michelson interferometer to deduce L_{opt} in the cell in which the pressure is varied



Pressure in the cell: 1 bar -> 0.1 mbar

-> *F* fringes on the photodiode

-> Path length L_0

$$(n-1)L_0 = F\,\frac{\lambda_a}{2}$$

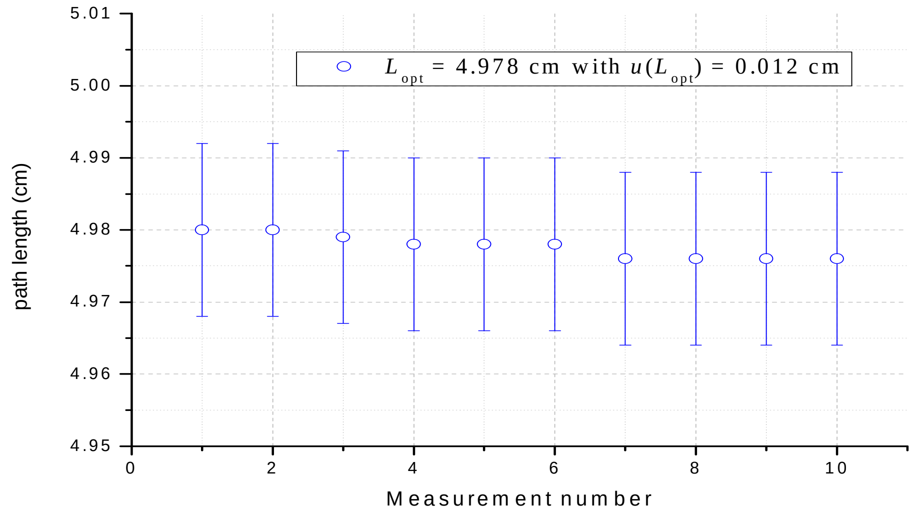
n	: index of refraction of air
L_0 / m	: light path length
F	: number of fringes
λ_a / m	: laser wavelength

Edlen formula for the air index of refraction at pressure *P* and temperature *T*

$$n-1 = \frac{p\cdot 10^{-8}\left[8342.54 + 2406147(130-\sigma^2)^{-1} + 15998(38.9-\sigma^2)^{-1}\right]\left[1+10^{-8}\cdot(0.601-0.00972T)\,p\right]}{96095.43\,(1+0.003661T)}$$

Absorption path length measurements by interferometry

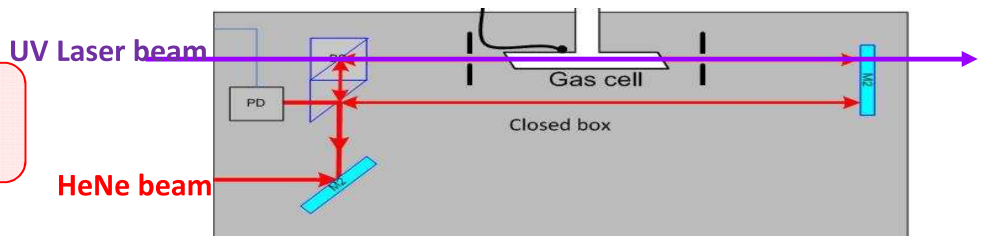
Measurements



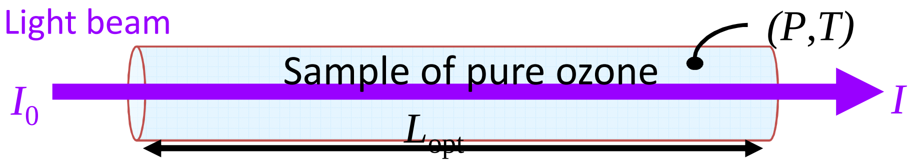
OK to be used for cross-section measurements, provided same laser path in the gas cell

Uncertainty budget

Quantity	Value	Standard Uncertainty
F	42	0.102
T	22.3 °C	0.018 °C
P_a	1003.25 hPa	0.852 Pa
λ_a	0.632823 µm	3.47×10^{-6} µm
λ_v	0.632991 µm	0.29×10^{-6} µm
L_{opt}	**4.979 cm**	**0.012 cm**



Ozone cross-section measurement principle



$$\sigma_{O3} = \frac{1}{L_{opt}} \frac{T}{P_{O_3}} \frac{R}{Na} \ln\left(\frac{I}{I_0}\right)$$

Pressure : pressure sensors measure total pressure P_T, not partial pressure $P_{O3} = x(O_3)\, P_T$

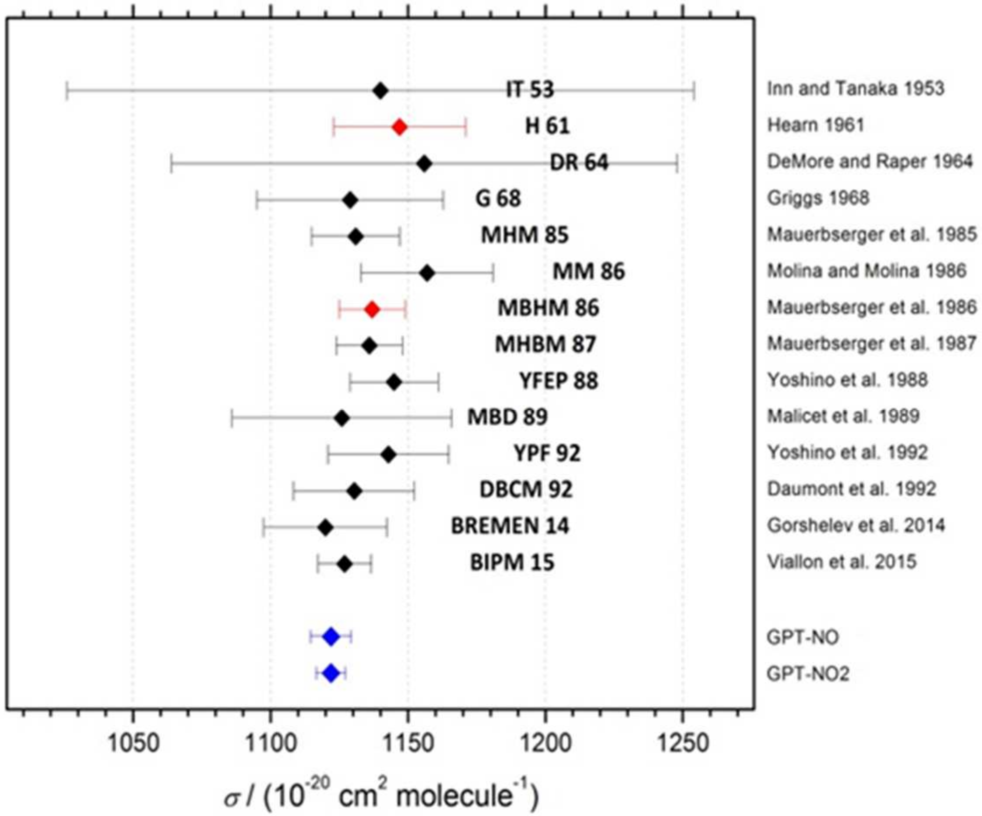
$$\sigma_{O3} = \frac{1}{L_{opt}} \frac{T}{P_T \cdot x(O_3)} \frac{R}{Na} \ln\left(\frac{I}{I_0}\right)$$

Purity = assessment of impurities

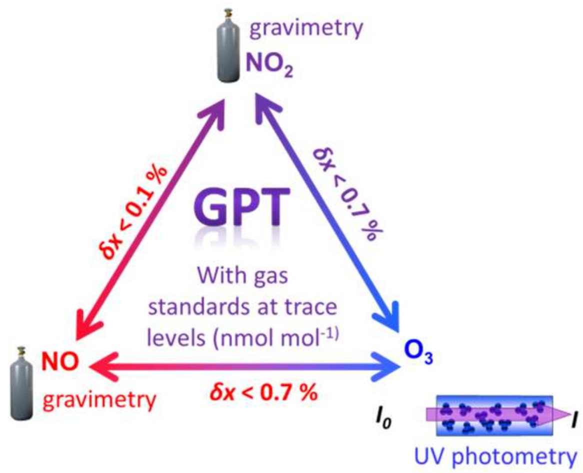
- condensables x_C
- non-condensables x_{NC}

$$\sigma_{O3} = \frac{1}{L_{opt}} \frac{T}{P_T \cdot \left[1 - \sum_i x_{NC} - \sum_i x_C\right]} \frac{R}{Na} \ln\left(\frac{I}{I_0}\right)$$

Comparison of methods



$$NO + O_3 \rightarrow NO_2 + O_2$$



Thank you.

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