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Standards and Scales for atmospheric CO_2 measurements: A new reference facility

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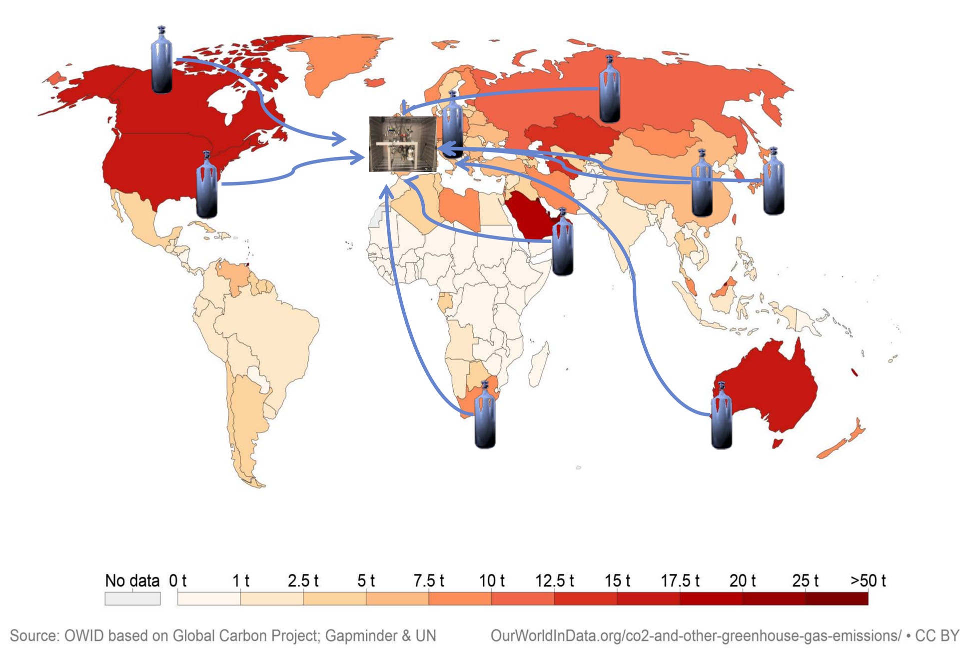
INTRODUCTION

BIPM.QM–K2, an on–going comparison to monitor the accuracy and uncertainty of primary CO_2 in air standards

- Efforts to constraint CO_2 emissions induce an increased number of monitoring stations
- Monitoring networks of CO_2 concentration in atmosphere need **accurate standards** with CO_2 mole fractions known to better than 0.03% relative uncertainty
- **Reference mixtures of CO_2 in air** from metrology institutes and central calibration facilities to be compared at BIPM
- BIPM central facility to consist of system to measure CO_2 in air by **manometry**



Map : CO_2 emissions per capita measured in tonnes per year, in 2016

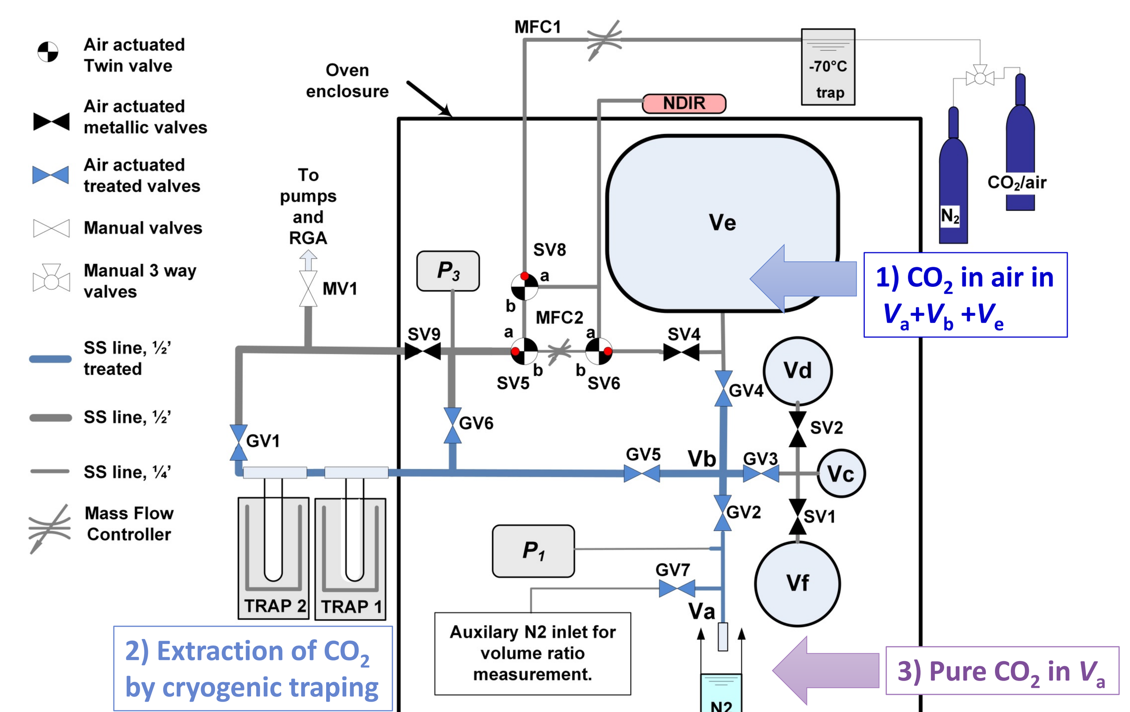
MEASUREMENT PRINCIPLE

- CO_2 mole fraction measurement by cryogenic separation from its air matrix
- CO_2 deduced from ratios of Pressure Temperature Volume between extracted CO_2 and air sample

$$x_{CO2} = \frac{V_2}{V_1}\left(\frac{P_{CO2}}{P_{air}}\right)\left(\frac{T_{air}}{T_{CO2}}\right)$$

$$V_1 = V_a + V_b + V_e = 6\ L$$

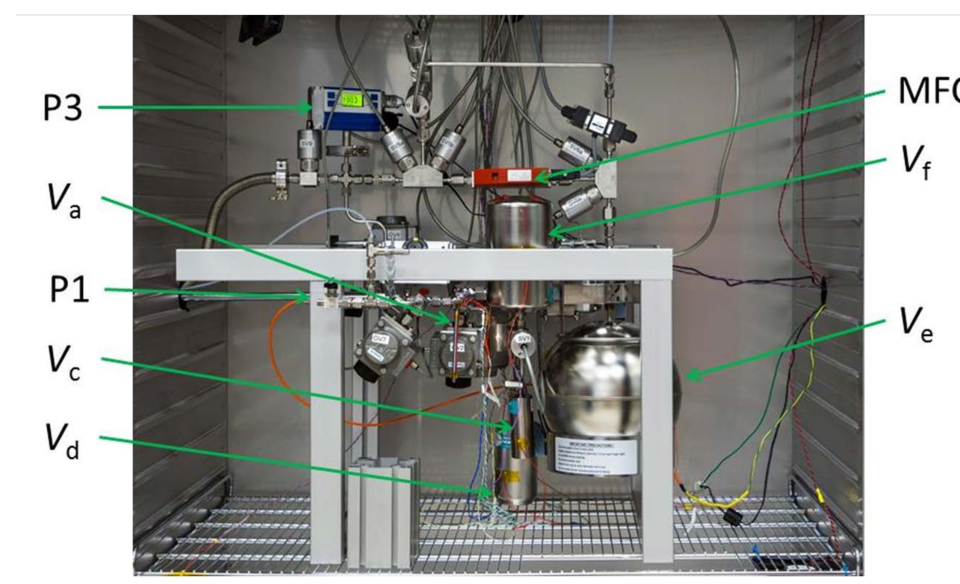
$$V_2 = V_a = 6\ mL$$



Flow chart of the CO_2-PVT system, with its containers inside an oven maintained at 40°C

INNOVATIVE SURFACE TREATMENT

- The system was built in stainless steel for mechanical stability
- Parts in contact with CO_2 were Silconert® treated to **minimise adsorptions**
- 3 auxilliaries vessels were added to allow a better **volume ratio** measurement



Volume ratio measured by series of expansions of inert gas in the 5 vessels, from the smallest to the biggest

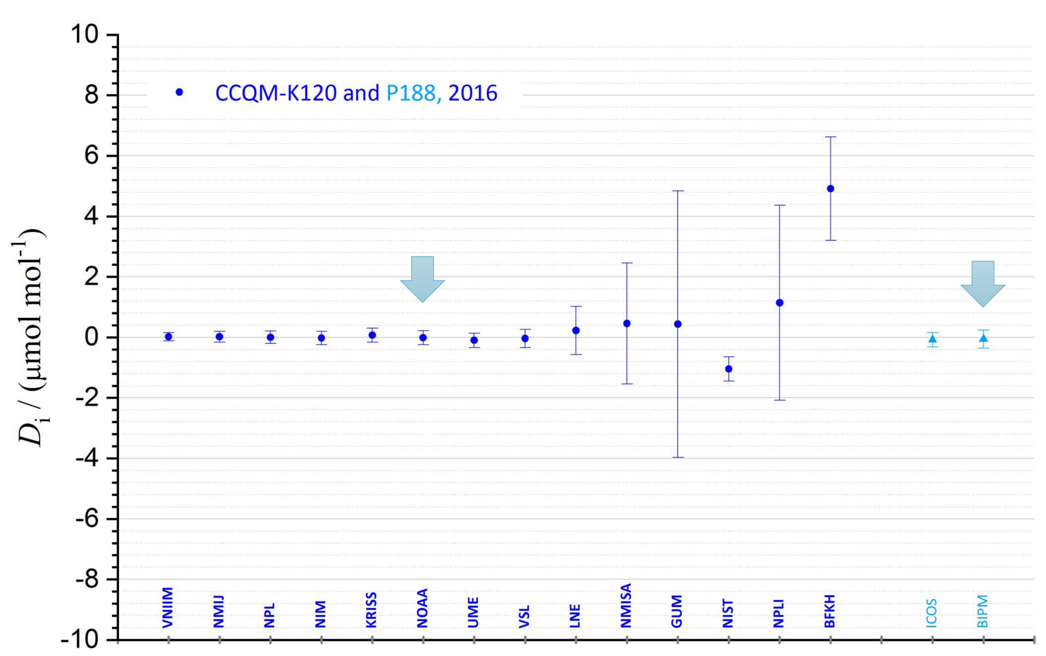
$$r_i = \frac{V_i}{V_{i+1}} = \frac{P_i}{P_{i+1}}$$

P_i close to atmo. Pressure
P_{i+1} close to 20 kPa

Picture of the CO_2-PVT system inside the oven

COMPARABILITY WITH OTHERS

- International comparison CCQM-K120/P188 performed by BIPM with 16 labs
- Comparison of reference mixtures prepared by **gravimetry**
- Included NOAA which maintain an **all-glass manometric** system



$D_i = x_{lab} - x_{ref}$

x_{lab} obtained by gravimetry except **NOAA** and **BIPM**

x_{ref} calculated from a calibration line defined by the ensemble

Results of the **2016-2017** international comparison of CO_2 in air standards at 380 µmol/mol

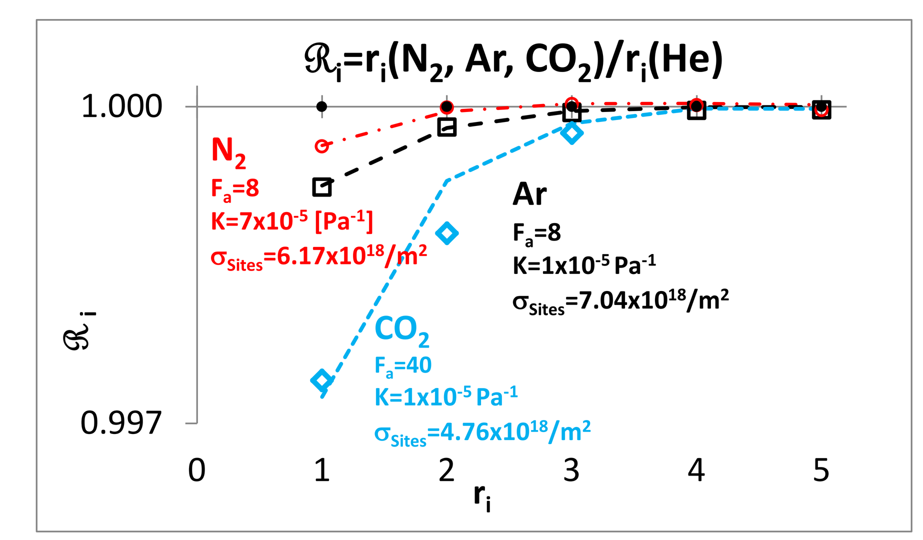
MEASUREMENT UNCERTAINTIES

- 2018 uncertainty budget includes several corrections
- **Most important** uncertainty comes from **volume ratio R_v**
- This triggered R_v measurements with several gases

Description	Symbol	Approximate Value	Standard Uncertainty	Contribution to $u(x_{CO2})/x_{CO2}$
Air temperature (type B)	T_{air}	313.5 K	0.01 K	3.2×10^{-5}
Air pressure (type B)	P_{air}	100000 Pa	2.3 Pa	2.3×10^{-5}
CO_2 temperature (type B)	T_{CO2}	313.5 K	0.01 K	3.2×10^{-5}
CO_2 pressure (type B)	P_{CO2}	25000 Pa	1.7 Pa	6.8×10^{-5}
Volume ratio meas.	R_v	658.9	0.19	2.9×10^{-4}
Virial function for air	γ_{air}	0.99982	6.2×10^{-6}	6.2×10^{-6}
Virial function for CO_2	γ_{CO2}	0.99894	2.4×10^{-6}	2.4×10^{-6}
N_2O Correction	x_{N2O}	325 nmol/mol	1.6 nmol/mol	4.2×10^{-6}
Repeatability of x_{CO2}	x_{CO2_rep}	380 µmol/mol	0.07 µmol/mol	2.0×10^{-4}
CO_2 escaping trap	x_{CO2_esc}	0 µmol/mol	0.04 µmol/mol	1.0×10^{-4}
CO_2 not transferred to V_s	x_{CO2_nt}	0 µmol/mol	0.02 µmol/mol	5.0×10^{-5}
Background pressure	P_b	14.2 Pa	2.3 Pa	9.2×10^{-5}
Total	x_{CO2}	**380 µmol/mol**	**0.15 µmol/mol (3.9×10^{-4} relative)**	

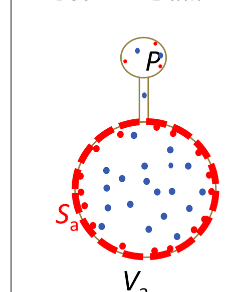
CO_2 ADSORPTION MODEL

- R_v shows **dependency on the gas**, mainly observed in $r_1 = V_a / V_b$
- Much worse with CO_2 than inert gases He, Ar or N_2
- Best explanation is **CO_2 adsorption on surfaces** inside the small volume V_a



Fit of minor volume ratios measurements with several gases using a Langmuir model

Total number of CO_2 molecules in V_a
$N_{Tot} = N_{Bulk} + N_{Ad}$

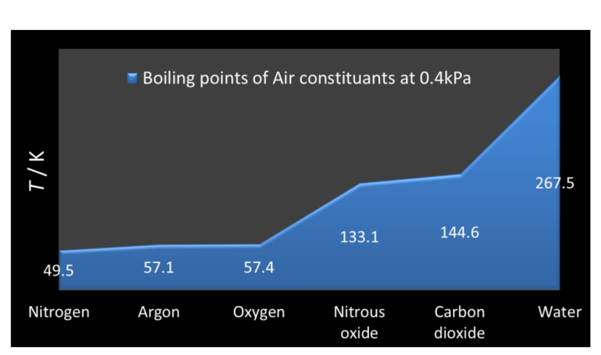


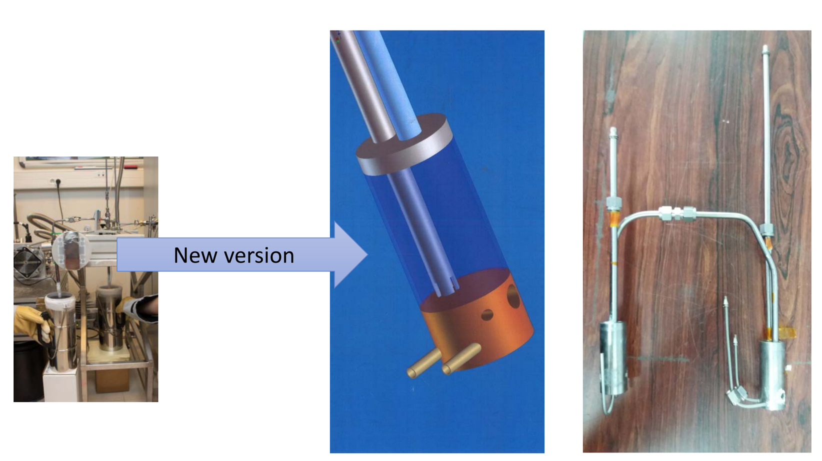
Number of « free » molecules
$N_{Bulk} = \frac{PV_a}{RT}$

Number of adsorbed molecules calculated with Langmuir model
$N_{ad} = \theta(P) S_a F_a \sigma_{sites}$
$\theta(P)$ fractional coverage of possible adsorptions sites $\theta(P) = \frac{KP}{1+KP}$
σ_{sites} density of adsorption sites
S_a surface
F_a surface enhancement factor

TRAPPING EFFICIENCY

- CO_2 trapping efficiency is a critical parameter; it needs to be maximized and traces of **un-trapped CO_2** estimated, as well as the **co-trapped compounds** H_2O and N_2O
- Twins traps are used to maximize CO_2 from H_2O separation; **automation** of the twins traps is under way to allow a better temperature control
- A residual gas analyser (mass spectrometer) was added to the setup to quantify traces of H_2O

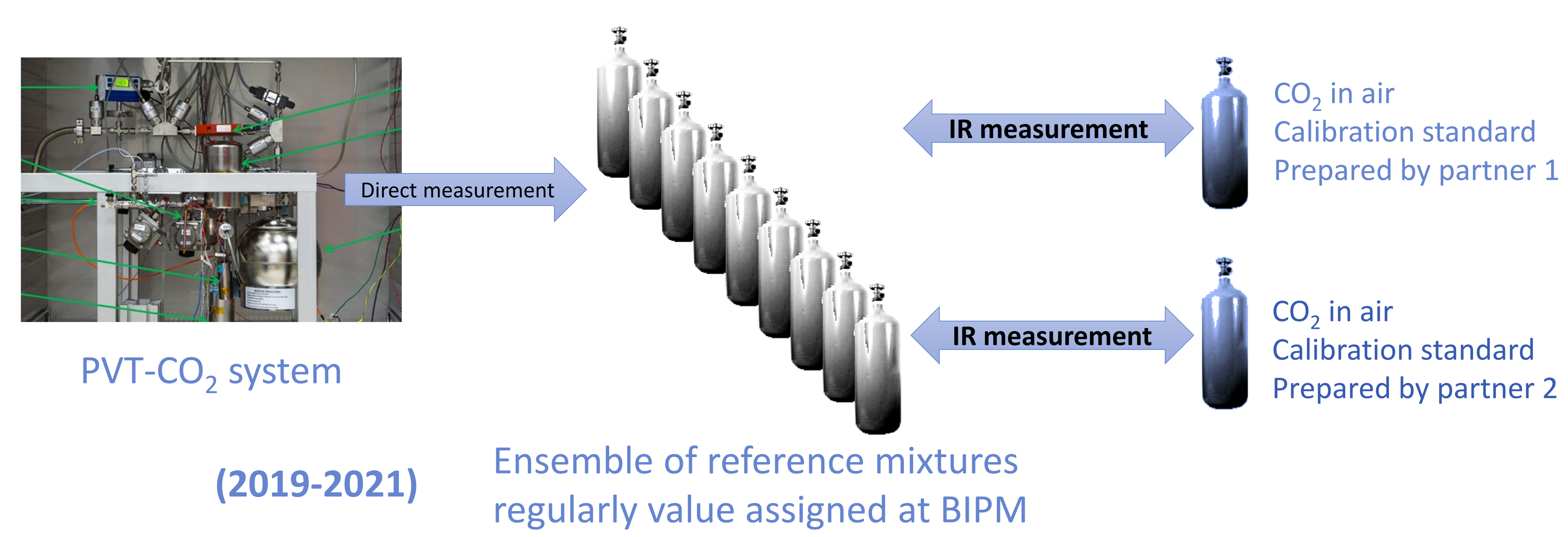




Twin traps, manual version being replaced by temperature controlled version

STABILITY TESTING OF THE FACILITY

- The CO_2-PVT system will value assign an ensemble of 2 times 9 reference mixtures
- Each ensemble to cover the range **380 µmol mol^{-1} to 800 µmol mol^{-1}**
- **Stability** of the CO_2-PVT **to be monitored** against the ensemble of standards and reference mixtures from partners



CONCLUSION

- A first version of the BIPM CO_2-PVT system was validated during the international comparison on CO_2 in air standards performed in 2016-2017 at 380µmol/mol
- Since then, the **uncertainties** associated with CO_2 mole fractions measurements by the manometric method **are being reduced** with a better understanding of the trapping efficiency as well as adsorption of CO_2 on the surfaces
- The system is being cheked for stability against an ensemble of 18 reference mixtures in the range 380-800 µmol/mol, in view of a future **on-demand comparison BIPM.QM-K2** with standards from National Metrology Institutes

Thanks to visiting scientists at BIPM:
S. Maxwell, C. Meyer, J. Schmidt, **NIST**, USA
F. Arrhen, **RISE**, Sweden

For further information

Please contact *jviallon@bipm.org*. More information on this and related projects can be obtained at *www.bipm.org*