Towards Standardized Whole Air and Purified Air Gas Production and Characterization for Greenhouse Gas Standards

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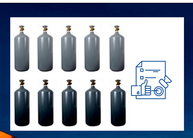
T2-A15

Theme 2: Accuracy requirements for atmospheric composition measurements across economic sectors, and temporal and spatial scales.

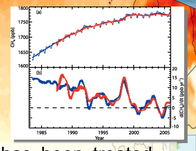
1. Background

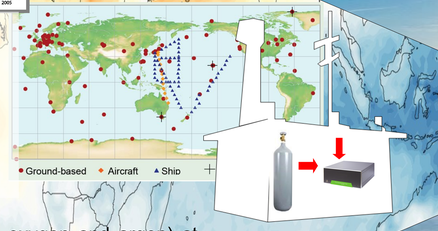


Greenhouse gas standards are used by the atmospheric community for monitoring amount fractions of greenhouse gases (GHGs).

GHG standards are predominantly produced using air matrix that is **sourced from:**

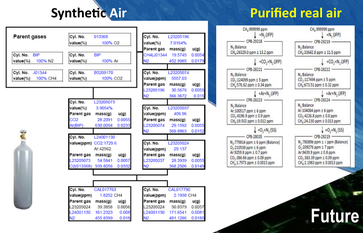
- whole air that has been treated with adsorbents or;
- relatively clean, whole air (also referred to as natural air), or;
- cryogenically purified of less volatile components (purified air) and compressed.





These processes should leave the major components of air (nitrogen, oxygen and argon) at ambient atmospheric levels so as not to introduce matrix effects that could bias measurements. Potential impacts to the minor component amount fractions are process dependent.

Example of real dilution scheme from pure gases to CH_4



2. Requirements for further development

The production processes have the advantage of being able to fill large cylinders providing greater amounts of calibrating gas for the user. The global production capacity for both whole air and purified air is limited, noting also that specialty gas producers almost uniquely manufacture gas standards by blending high purity gases rather than by adding components to purified air.

Purified air: potential issues that can be, and on occasion, have been reported are significant deviations in the amount fractions of major components in the air, argon amount fraction for example, and large variations in levels of minor components, such as nitrous oxide, carbon tetrafluoride, sulfur hexafluoride, carbon dioxide and the heavy noble gases.

Whole air: it is important that its composition is controlled and can be produced with both major and minor components, including water vapour, within well-defined tolerance limits.

- production is predominantly limited to small-scale,
- research-oriented facilities,
- typically utilizing a breathing-air compressor that is no longer manufactured.

Fixed limits for balance gas composition in standards submitted for the comparison. Based upon the possible biases that could be introduced into the spectroscopic comparison methods due to variation in the composition of the air matrix in different standards, participating laboratories were asked to ensure that the composition of their air matrix was within these limits.

1. Work towards increase availability of high quality purified air/whole air matrix gases
2. Define acceptable tolerance limits for the composition of these gases
3. Define performance of measurement methods required to verify these limits
4. Involve standards writing organizations to facilitate uptake by specialty gas industry

Future activities will focus on working with the atmospheric monitoring community, WMO Central Calibrations Laboratories, National Metrology Institutes, and Specialty Gas Producers in agreeing and publishing acceptable tolerance limits for the composition of air matrix gas, and the performance of measurement methods required to verify this.

4. Recommendations:

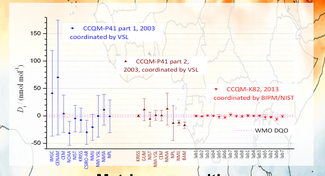
This output will provide a significant step forward to the final desired outcome of increased availability, accessibility and affordability of quality assured gas standards for a broad range of GHG measurements.

Standardization

Standardized requirements for the composition of both purified air and whole air matrix gas, would be an important step to increasing the availability and accessibility of GHG standards.

3. Matrix Air composition used for two successful International comparisons

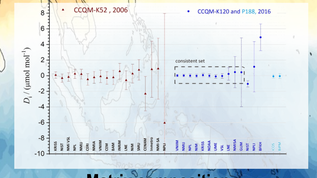
CCQM-K82 CH_4 comparison



Matrix composition

Component in Air	Minimum mole fraction permitted within submitted cylinder	Maximum mole fraction permitted within submitted cylinder
N_2	0.7784 mol/mol	0.7831 mol/mol
O_2	0.2077 mol/mol	0.2111 mol/mol
Ar	8.8 mmol/mol	9.8 mmol/mol
CO_2	360 µmol/mol	400 µmol/mol

CCQM-K120 CO_2 comparison



Matrix composition

Component in Air	Minimum mole fraction permitted within	Maximum mole fraction permitted within
N_2	0.7804 mol/mol	0.7814 mol/mol
O_2	0.2088 mol/mol	0.209 mol/mol
Ar	8.9 mmol/mol	9.7 mmol/mol
CH_4	0 nmol/mol	1900 nmol/mol
N_2O	0 nmol/mol	330 nmol/mol

CCQM-K120.a matrix composition limit values(380 µmol /mol and 480 µmol/mol CO_2 in air‡).

Component in Air	Minimum mole fraction permitted within submitted cylinder	Maximum mole fraction permitted within submitted cylinder
N_2	0.7789 mol/mol	0.7829 mol/mol
O_2	0.2073 mol/mol	0.2113 mol/mol
Ar	7.8 mmol/mol	10.8 mmol/mol
CH_4	0 nmol/mol	1900 nmol/mol
N_2O	0 nmol/mol	330 nmol/mol

CCQM-K120.b matrix composition limits values(480 µmol/mol and 800 µmol/mol CO_2 in air‡)(‡3 standards in total).