Gaseous Reference Materials to Underpin Measurements of Amount Fraction and Isotopic Composition of Greenhouse Gases

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The European Metrology Research Programme HIGHGAS project has led to significant advances in the development of high accuracy, SI traceable, gaseous reference materials of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and carbon monoxide (CO). Research has focussed on driving the uncertainty of the reference materials towards the World Meteorological Organization (WMO) compatibility goals and monitoring their stability. Improvements have been achieved by optimising passivation chemistry used in cylinder treatment, reducing the uncertainty in the gravimetry of the matrix components and making high-accuracy quantification of target impurities in the matrix gas.

In addition, a capability to fully characterise the isotopic composition of the CO_2 in the reference materials has been developed to account for measurement biases introduced by instrumentation detecting only certain isotopologues. The data shows that knowledge of the CO_2 composition is crucial for addressing commutability issues from preparing synthetic reference materials but also for assigning the correct atomic weight for the calculation of gravimetrically prepared mixtures, which can change the amount fraction by as much as 4.4 nmol/mol.

This work has provided the framework for new research priorities focussed on developing gaseous reference materials of CO_2 and N_2O for underpinning measurements of stable isotopes to infer their origin in the atmosphere. A new infrastructure is proposed that will deliver international CO_2 reference materials with traceability to the VPDB primary standard, to meet the increasing demand. New international gaseous N_2O reference materials will also be developed with stated uncertainties. The research will develop new field-deployable spectroscopy and initiate SI traceability of the international CO_2 isotope ratio scale by re-measuring the absolute isotope ratios by gas-source isotope ratio mass spectrometry (IRMS).

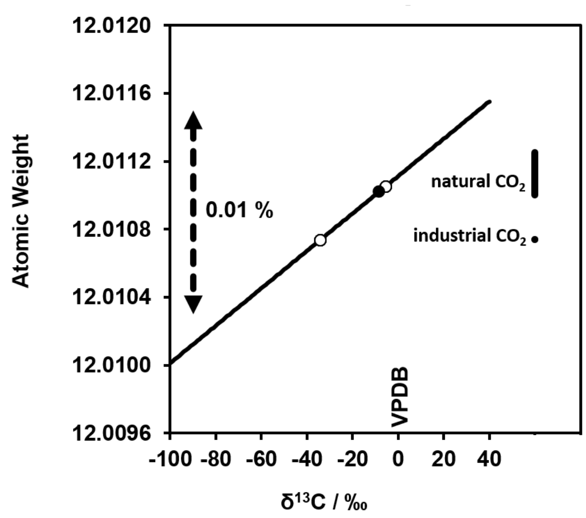

Figure 1. Atomic weight of carbon plotted as a function of the proportion of ^{13}C present, denoted by the delta scale, where VPDB has a $\delta^{13}C$ value of zero. The difference in atomic weight for naturally occurring CO_2 compared to the CO_2 purified by an industrial process is shown and their difference on the δ scale. The filled circle shows the measurement of a standard referenced to the WMO scale using IRMS. The open circles show IRMS measurements of the CO_2 purified by an industrial process (with the most negative δ value) and the same gas spiked with pure $^{13}CO_2$, both diluted to ambient amount fractions with synthetic air.