



A synthetic zero air standard

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We present work towards providing traceability for measurements of high impact greenhouse gases identified by the World Meteorological Organisation (WMO) as critical for global monitoring. Standards for these components are required with challengingly low uncertainties to improve the quality assurance and control processes used for the global networks to better assess climate trends. Currently the WMO compatibility goals require reference standards with uncertainties of $< 100 \text{ nmolmol}^{-1}$ for CO_2 (northern hemisphere) and $< 2 \text{ nmolmol}^{-1}$ for CH_4 and CO .

High purity zero gas is required for both the balance gas in the preparation of reference standards and for baseline calibrations of instrumentation. Quantification of the amount fraction of the target components in the zero gas is a significant contributor to the uncertainty and is challenging due to limited availability of reference standard at the amount fraction of the measurand and limited analytical techniques with sufficient detection limits.

A novel dilutor was used to blend NPL Primary Reference Gas Mixtures containing CO_2 , CH_4 and CO at atmospheric amount fractions with a zero gas under test. Several mixtures were generated with nominal dilution ratios ranging from 2000:1 to 350:1. The baseline of two cavity ring down spectrometers was calibrated using the zero gas under test after purification by oxidative removal of CO and hydrocarbons to $< 1 \text{ nmolmol}^{-1}$ (SAES PS15-GC50) followed by the removal of CO_2 and water vapour to $< 100 \text{ pmolmol}^{-1}$ (SAES MC190). Using the standard addition method.[1] we have quantified the amount fraction of CO , CO_2 , and CH_4 in scrubbed whole air (Scott Marrin) and NPL synthetic zero air. This is the first synthetic zero air standard with a matrix of N_2 , O_2 and Ar closely matching ambient composition with gravimetrically assigned values and with accurate quantification of the CO , CO_2 , and CH_4 impurities.

[1] Brown, R.J.C et al., *Analytica Chimica Acta* 587, 158-163 (2007)