

Calibration standards for major greenhouse gases and carbon monoxide: status and challenges.

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Human influence on increasing greenhouse gas mole fractions in the atmosphere and effects on positive radiative forcing as well as observed global warming and sea level rise are well accepted [1]. For interpretation of global or continental scale greenhouse gas data, obtained from different laboratories, measurement results have to coincide within compatibility goals set by the World Meteorological Organization (WMO) [2]. Despite significant advances in measurement techniques [3], WMO compatibility goals are regularly missed, shown by round-robin experiments of standard gases and comparisons of field samples or parallel measurements. Therefore, precise and accurate calibration using standards with good long-term stability is needed to reduce uncertainties of atmospheric measurements.

This is addressed by the WMO Global Atmosphere Watch Programme (GAW), where Central Calibration Laboratories (CCLs) maintain calibration scales to ensure consistency of measurements within the network to primary reference materials. Furthermore, participating GAW laboratories are supported by World Calibration Centres (WCCs) performing audits and organizing round-robin comparisons. The CCL participates regularly in comparisons with independent primary scales to assure traceability of established primary reference materials to fundamental quantities (SI) [e.g. 4].

Within the European Metrology Research Programme (EMRP) ENV52 project “Metrology for high-impact greenhouse gases” (HIGHGAS), static and dynamic primary reference gas mixtures for ambient levels of CO₂, CH₄, N₂O and CO in air were prepared by different National Metrology Institutes (NMIs). In order to progress beyond the state of the art, research focused on improving passivation chemistry, quantification of target impurities in the air matrix, and determining the isotopic composition. These primary reference gas mixtures were compared in a round robin experiment against standards calibrated against reference gases currently used by the GAW community.

We will show results of the comparison of the HIGHGAS and the WMO reference standards, and put this into the context of the WMO/GAW quality management framework.

[1] IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

[2] WMO: 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17 September 2015, GAW Report No. 229, World Meteorological Organization, Geneva, Switzerland, 2016.

[3] Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M., Kozlova, E., Spain, T. G., Steinbacher, M., van der Schoot, M. V., and Buchmann, B.: Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, *Atmos. Meas. Tech.*, 9, 4737-4757, 2016.

[4] Flores, E., Viallon, J., Choteau, T., Moussay, P., Wielgosz, R., Kang, N., Kim, B. M., Zalewska, E., van der Veen, A., Konopelko, L., Wu, H., Han, Q., Rhoderick, G., Guenther, F. R., Watanabe, T., Shimosaka, T., Kato, K., Hall, B., and Brewer, P.: International comparison CCQM-K82: methane in air at ambient level (1800 to 2200) nmol/mol, *Metrologia*, 52, 08001, 2015.

